

# Supporting Information

## Catalytic Enantioselective Radical Coupling of Activated Ketones with *N*-Aryl Glycines

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## 1. General information

### General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reaction mixtures were stirred in 10 mL sample vial with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed *in vacuo* under ~30 mmHg and heated with a water bath at 30–35 °C using rotary evaporator with aspirator. The condenser was cooled with running water at 0 °C.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F<sub>254</sub>. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining Ce(SO<sub>4</sub>)<sub>2</sub> and anisaldehyde solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained *silica gel* 200–300 mesh. Columns were packed as slurry of *silica gel* in petroleum ether and equilibrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2 atm with an air pump.

### Instrumentations

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) and carbon NMR (<sup>13</sup>C NMR) were recorded in CDCl<sub>3</sub> otherwise stated. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: CDCl<sub>3</sub> (<sup>1</sup>H NMR: δ 7.26, singlet; <sup>13</sup>C NMR: δ 77.16, triplet). Multiplicities were given as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quintet*, *m* (multiplets), *dd* (doublet of doublets), *dt* (doublet of triplets), and *br* (broad). Coupling constants (*J*) were recorded in Hertz (Hz). The number of proton atoms (*n*) for a given resonance was indicated by *n*H. The number of carbon atoms (*n*) for a given resonance was indicated by *n*C. HRMS (Analyzer: TOF) was reported in units of mass of charge ratio (*m/z*). Mass samples were dissolved in CH<sub>3</sub>CN (HPLC Grade) unless otherwise stated.

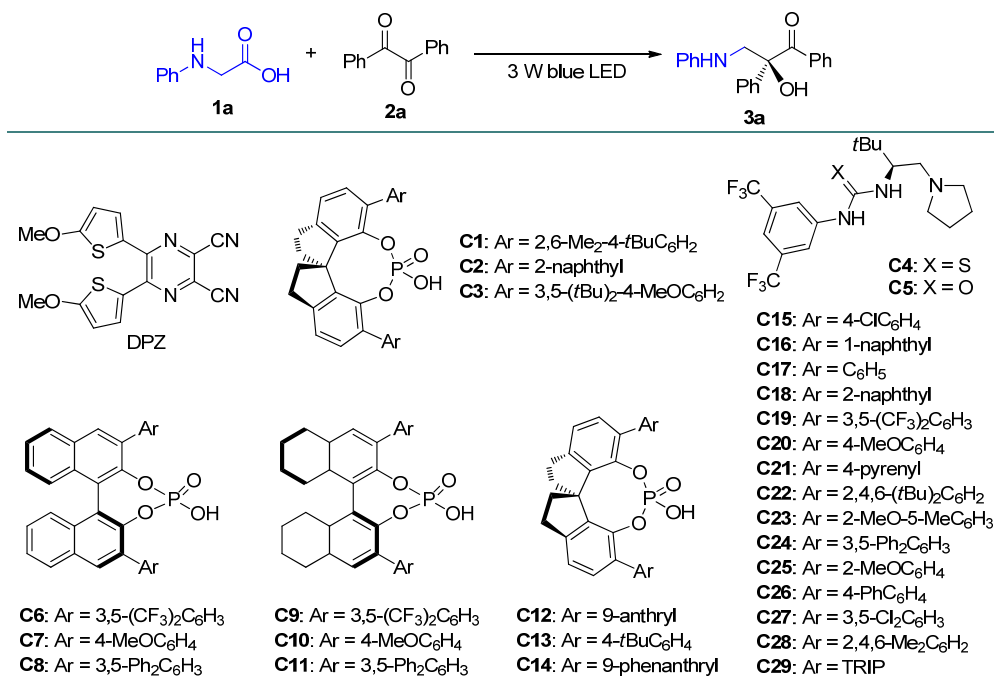
Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm and reported as follows;  $[\alpha]_{\lambda}^{T^{\circ}C}$  ( $c = \text{g}/100 \text{ mL}$ , solvent). Melting points were determined on a melting point apparatus.

Enantiomeric excesses were determined by chiral High Performance Liquid Chromatography (HPLC) analysis. UV detection was monitored at 254 nm and 210 nm at the same time. HPLC samples were dissolved in HPLC grade isopropanol (IPA) unless otherwise stated.

### **Materials**

All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified. All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc) were distilled. Anhydrous DCM,  $\text{CH}_3\text{CN}$  were freshly distilled from  $\text{CaH}_2$  and stored under  $\text{N}_2$  atmosphere. THF,  $\text{Et}_2\text{O}$ , MTBE, 1,2-dimethoxyethane, CPME, and toluene were freshly distilled from sodium/benzophenone before use. All compounds synthesized were stored in a  $-20\text{ }^{\circ}\text{C}$  freezer and light-sensitive compounds were protected with aluminium foil.

## 2. Optimization of reaction conditions

Table S1. Optimization of Reaction Conditions.<sup>a</sup>

Entry	PC (mol%)	Cat.	Solvent	<i>T</i> (°C)	Additive (equiv/mg)	ee (%) <sup>b</sup>
1	DPZ [1.0]	--	CH <sub>2</sub> Cl <sub>2</sub>	25	--	-- <sup>c</sup>
2	DPZ [1.0]	<b>C4</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	0
3	DPZ [1.0]	<b>C5</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	0
4	DPZ [1.0]	<b>C6</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	7
5	DPZ [1.0]	<b>C7</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	12
6	DPZ [1.0]	<b>C8</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	34
7	DPZ [1.0]	<b>C9</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	18
8	DPZ [1.0]	<b>C10</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	16
9	DPZ [1.0]	<b>C11</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	23
10	DPZ [1.0]	<b>C12</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	36
11	DPZ [1.0]	<b>C13</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	2
12	DPZ [1.0]	<b>C14</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	45
13	DPZ [1.0]	<b>C15</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	11
14	DPZ [1.0]	<b>C16</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	18
15	DPZ [1.0]	<b>C17</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	15
16	DPZ [1.0]	<b>C18</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	15
17	DPZ [1.0]	<b>C19</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	32
18	DPZ [1.0]	<b>C20</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	11
19	DPZ [1.0]	<b>C21</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	--	24
20	DPZ [1.0]	<b>C14</b>	Et <sub>2</sub> O	25	--	41
21	DPZ [1.0]	<b>C14</b>	Tol.	25	--	40
22	DPZ [1.0]	<b>C14</b>	CH <sub>3</sub> CN	25	--	61
23	DPZ [1.0]	<b>C22</b>	CH <sub>3</sub> CN	25	--	65
24	DPZ [1.0]	<b>C23</b>	CH <sub>3</sub> CN	25	--	41

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25	DPZ [1.0]	<b>C24</b>	CH <sub>3</sub> CN	25	--	51
26	DPZ [1.0]	<b>C25</b>	CH <sub>3</sub> CN	25	--	41
27	DPZ [1.0]	<b>C26</b>	CH <sub>3</sub> CN	25	--	27
28	DPZ [1.0]	<b>C27</b>	CH <sub>3</sub> CN	25	--	33
29	DPZ [1.0]	<b>C28</b>	CH <sub>3</sub> CN	25	--	62
30	DPZ [1.0]	<b>C28</b>	THF	25	--	67
31	DPZ [1.0]	<b>C28</b>	DCM	25	--	57
32	DPZ [1.0]	<b>C28</b>	Tol.	25	--	44
33	DPZ [1.0]	<b>C28</b>	Et <sub>2</sub> O	25	--	66
34	DPZ [1.0]	<b>C28</b>	CPME	25	--	69
35	DPZ [1.0]	<b>C28</b>	MTBE	25	--	70
36	DPZ [1.0]	<b>C28</b>	MTBE	10	--	74
37	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg)	80
38	DPZ [1.0]	<b>C28</b>	MTBE	10	4Å MS (25 mg)	78
39	DPZ [1.0]	<b>C28</b>	MTBE	10	3Å MS (25 mg)	68
40	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (35 mg)	75
41	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + K <sub>3</sub> PO <sub>4</sub> (0.2 equiv)	23
42	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + K <sub>2</sub> HPO <sub>4</sub> (0.2 equiv)	80
43	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + KH <sub>2</sub> PO <sub>4</sub> (0.2 equiv)	80
44	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + KPF <sub>6</sub> (0.2 equiv)	82
45	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + NaPF <sub>6</sub> (0.2 equiv)	82
46	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + LiPF <sub>6</sub> (0.2 equiv)	80
47	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + LiBF <sub>4</sub> (0.2 equiv)	75
48	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + NaBARF (0.2 equiv)	79
49	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + NaOAc (0.2 equiv)	78
50	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + PhCO <sub>2</sub> Na (0.2 equiv)	75
51	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + NaF (0.2 equiv)	82
52	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + NaBr (0.2 equiv)	82
53	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	85
54	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (0.2 equiv)	81
55	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + NaI (0.2 equiv)	80
56	DPZ [1.0]	<b>C28</b>	MTBE	10	5Å MS (25 mg) + KBr (0.2 equiv)	77
57	DPZ [1.0]	<b>C28</b>	MTBE	20	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	80
58	DPZ [1.0]	<b>C28</b>	MTBE	15	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	81
59	DPZ [1.0]	<b>C28</b>	MTBE	0	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	68
60	DPZ [1.0]	<b>C28</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	87
61	DPZ [1.5]	<b>C28</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	88
62	DPZ [2.0]	<b>C28</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	88
63	DPZ [1.5]	<b>C28</b>	CPME	10	5Å MS (25 mg) + TBAB (0.3 equiv)	87
64	DPZ [1.5]	<b>C28</b>	CPME	10	5Å MS (25 mg) + TBAC (0.3 equiv)	85
65	DPZ [1.5]	<b>C28</b>	CPME	10	5Å MS (25 mg) + TBAI (0.3 equiv)	85
66	DPZ [1.5]	<b>C28</b>	CPME	10	5Å MS (25 mg) + TOAB (0.3 equiv)	87
67	DPZ [1.5]	<b>C28</b>	CPME	10	5Å MS (25 mg) + TBAB (0.5 equiv)	88
68	DPZ [1.5]	<b>C28</b>	CPME	10	5Å MS (25 mg) + TBAB (1.0 equiv)	87

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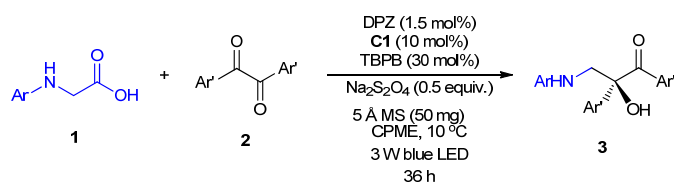
69	DPZ [1.5]	<b>C1</b>	CPME	10	5Å MS (25 mg) + TBAB (0.3 equiv)	89
70	DPZ [1.5]	<b>C1</b>	CPME	10	5Å MS (25 mg) + TBPB (0.3 equiv)	90
71	DPZ [1.5]	<b>C1</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.2 equiv)	88
72	DPZ [1.5]	<b>C1</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.5 equiv)	89
73	DPZ [1.5]	<b>C1</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (1.0 equiv)	88
74	DPZ [1.5]	<b>C1</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.5 equiv) + TBPB (0.3 equiv)	93 <sup>d</sup>
75	DPZ [1.5]	<b>C2</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.5 equiv) + TBPB (0.3 equiv)	76
76	DPZ [1.5]	<b>C3</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.5 equiv) + TBPB (0.3 equiv)	67
77	DPZ [1.5]	<b>C29</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.5 equiv) + TBPB (0.3 equiv)	72 <sup>e</sup>
78	Ru <sup>2+</sup> [1.5] <sup>f</sup>	<b>C3</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.5 equiv) + TBPB (0.3 equiv)	89
79	RB [1.5] <sup>g</sup>	<b>C3</b>	CPME	10	5Å MS (25 mg) + Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> (0.5 equiv) + TBPB (0.3 equiv)	91

<sup>a</sup> Reaction conditions: **1a** (0.075 mmol), **2a** (0.05 mmol), chiral catalyst (10 mol%), degassed solvent (1.0 mL), irradiation with blue LED (3 W, 450 nm), 12–36 h. <sup>b</sup> Determined by HPLC analysis on a chiral stationary phase. <sup>c</sup> Yield = 62% (Isolated by flash column chromatography on *silica gel*). <sup>d</sup> Yield = 78% (Isolated by flash column chromatography on *silica gel*). <sup>e</sup> Yield = 76% (Isolated by flash column chromatography on *silica gel*). <sup>f</sup> Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·6H<sub>2</sub>O. <sup>g</sup> RB = Rose Bengal.

### 3. General experimental procedures

#### (1) General procedure for asymmetric radical–radical cross–coupling of *N*-aryl glycines

##### 1 with 1,2-diketones 2

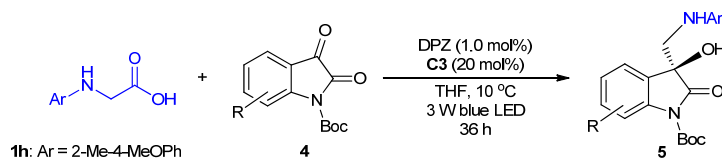


106.3  $\mu$ L (0.0015 mmol, 0.015 equiv) of DPZ solution (1.0 mg of DPZ in 200  $\mu$ L of toluene) was added into a 10 mL Schlenk tube, and then solvent was removed in *vacuo*. Subsequently, **1** (0.15 mmol, 1.5 equiv), **2** (0.10 mmol, 1.0 equiv), **C1** (0.01 mmol, 0.10 equiv), TBPB (0.03 mmol, 0.3 equiv), Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (0.05 mmol, 0.5 equiv), 5 Å MS (50 mg) and CPME (2.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at 10 °C (the temperature was maintained in an incubator) and in dark for 30 min, then irradiated by a 3 W blue LED ( $\lambda = 450\text{--}455$  nm) from a 2.0 cm distance for another 36 h. The reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (100/1–50/1 ratio). Removing the solvent in *vacuo*, afforded products **3a–3q**.

For product **3r**, the procedure is similar but with the following reaction conditions: **1** (0.15 mmol), **2** (0.1 mmol), DPZ (1.5 mol%), **C2** (10 mol%), 4 Å MS (50 mg), CPME (2.0 mL),  $-5$  °C, degassed and under an argon atmosphere, 36 h.

#### (2) General procedure for asymmetric radical–radical cross–coupling of *N*-aryl glycine

##### 1h with isatins 4



70.9  $\mu$ L (0.001 mmol, 0.01 equiv) of DPZ solution (1.0 mg of DPZ in 200  $\mu$ L of toluene) was added into a 10 mL Schlenk tube, and then solvent was removed in *vacuo*. Subsequently, **1h** (0.15 mmol, 1.5 equiv), **4** (0.10 mmol, 1.0 equiv), **C3** (0.02 mmol, 0.2 equiv) and THF (2.0 mL) were sequentially added, degassed three times by freeze-pump-thaw method. The reaction mixture was stirred under an argon atmosphere at 10 °C (the temperature was maintained in an incubator) and in dark for 30 min, then irradiated by a 3 W blue LED ( $\lambda =$

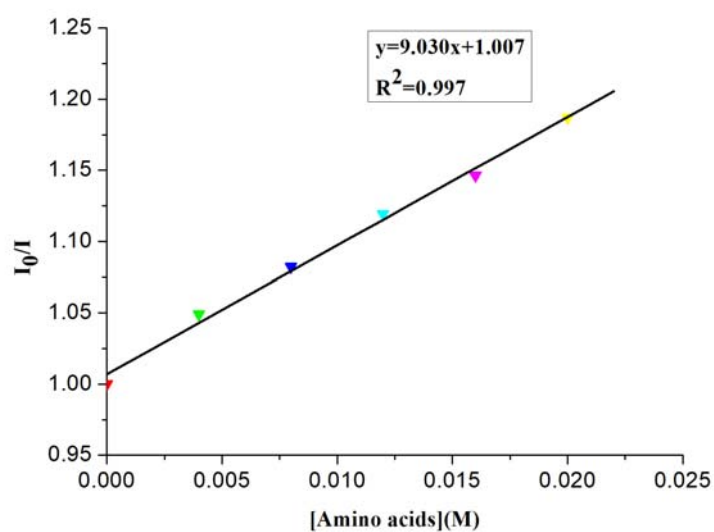


450–455 nm) from a 5.0 cm distance for another 36 h. The reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (80/1–5/1 ratio). Removing the solvent in *vacuo*, afforded products **5a–5l**.

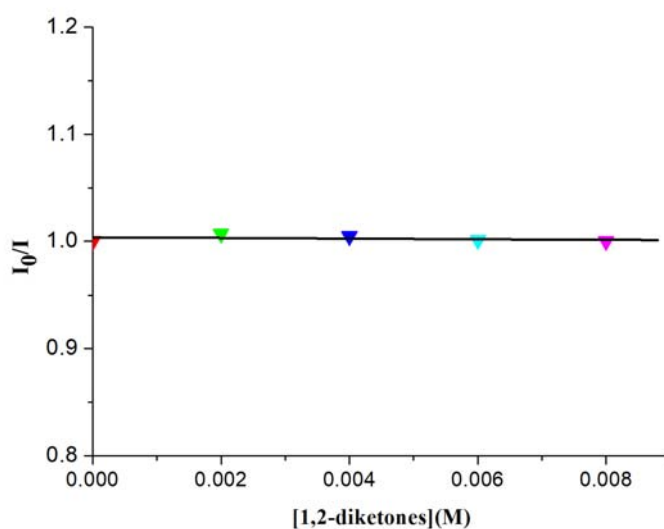
#### 4. Mechanism studies

##### Emission quenching experiments

Emission intensities were recorded on a spectrofluorometer. DPZ solution was excited at 448 nm and the emission intensity at 544 nm was observed. The appropriate amount of quencher was added to a solution of DPZ ( $5.0 \times 10^{-5}$  M) in CPME in 5.0 mL volumetric flask under  $N_2$ . The solution was transferred to a 1.5 mL quartz cell and the emission spectrum of the sample was collected.

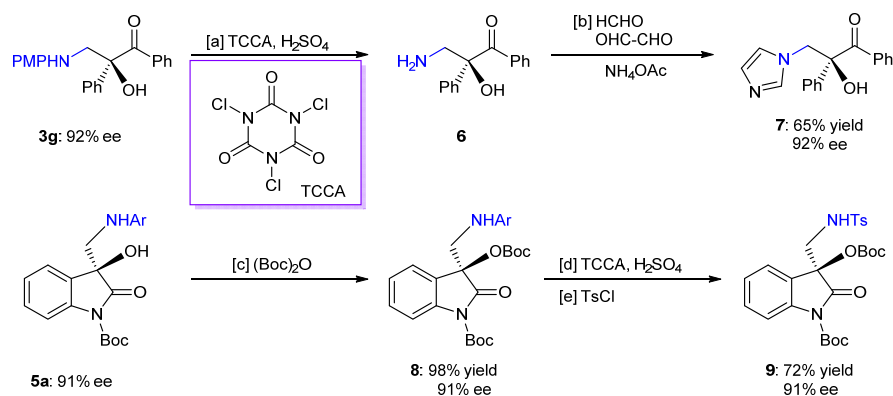


**Fig. S1.** Stern–Volmer quenching experiment of DPZ and **1a**.



**Fig. S2.** Stern–Volmer quenching experiment of DPZ and **2a**. No quenching observed.

## 5. Procedures of synthetic applications



**Step A:** To a solution of **3g** (0.4 mmol, 1.0 equiv) in 4.0 mL acetonitrile and 4.0 mL water, TCCA (0.2 mmol, 0.5 equiv) and 0.4 mL H<sub>2</sub>SO<sub>4</sub> (1.0 M) were added at 0 °C. The mixture was stirred for 16 h at room temperature. After removal of acetonitrile by evaporation, the resulting aqueous phase washed with 4.0 mL CH<sub>2</sub>Cl<sub>2</sub> for three times. The resulting aqueous phase was subsequently regulated to pH 11.0 through addition of saturated Na<sub>2</sub>CO<sub>3</sub> solution. The aqueous solution was extracted with 5.0 mL EtOAc for three times. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo* afforded product **6**, which was used for the next step without further purification.

**Step B:** Product **6**, glyoxal (0.8 mmol, 2.0 equiv), formaldehyde (0.8 mmol, 2.0 equiv), ammonium chloride (0.8 mmol, 2.0 equiv) was dissolved in methanol (0.5 mL). The reaction was heated at 80 °C for 5 h. After cooling to room temperature, the solvent was evaporated, NaOH (2.0 N, aq.) was added and the product was extracted with DCM (5 x 5 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in *vacuo*. The reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with dichloromethane/methanol (100/1–30/1 ratio). Removing the solvent in *vacuo*, afforded product **7** in 65% of yield over two steps and with 92% ee.

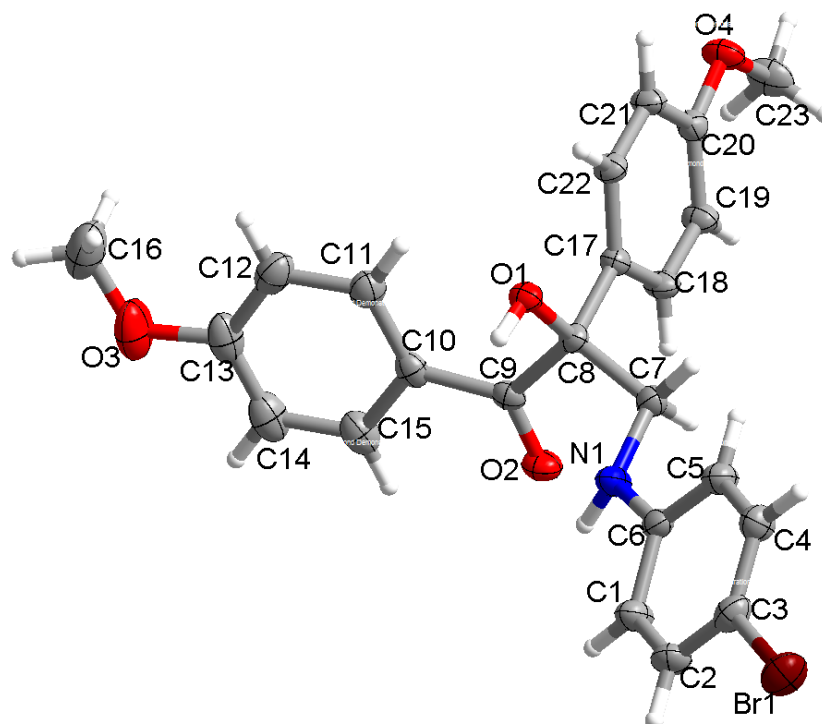
**Step C:** To a solution of **5a** (0.4 mmol, 1.0 equiv) in 4.0 mL DCM, DMAP (0.08 mmol, 0.2 equiv) and di-*tert*-butyl dicarbonate (0.44 mmol, 1.1 equiv) were added at 0 °C. The mixture was stirred for 0.5 h at room temperature. The reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (30/1–20/1 ratio). Removing the solvent in *vacuo*, afforded product **8** in 98% yield.

**Steps D and E:** To a solution of **8** (0.4 mmol, 1.0 equiv) in 4.0 mL acetonitrile and 4.0 mL

water, TCCA (0.2 mmol, 0.5 equiv) and 0.4 mL H<sub>2</sub>SO<sub>4</sub> (1.0 M) were added at 0 °C. The reaction worked for 16 h at room temperature. The reaction mixture was subsequently regulated to pH 11.0 through adding saturated Na<sub>2</sub>CO<sub>3</sub> solution. The aqueous solution was extracted with 5.0 mL EtOAc for three times. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in *vacuo*. The ethyl acetate solution of amine was cooled to 0 °C, and then triethylamine (0.8 mmol, 2.0 equiv) with 4-tosyl chloride (0.8 mmol, 2.0 equiv) were added. The reaction was stirred for 5 h at room temperature. The reaction mixture was directly loaded onto a short *silica gel* column, followed by gradient elution with petroleum ether/ethyl acetate (30/1–5/1 ratio). Removing the solvent in *vacuo*, afforded product **9** in 72% of yield over two steps and with 91% ee.

## 6. Determination of the absolute configurations

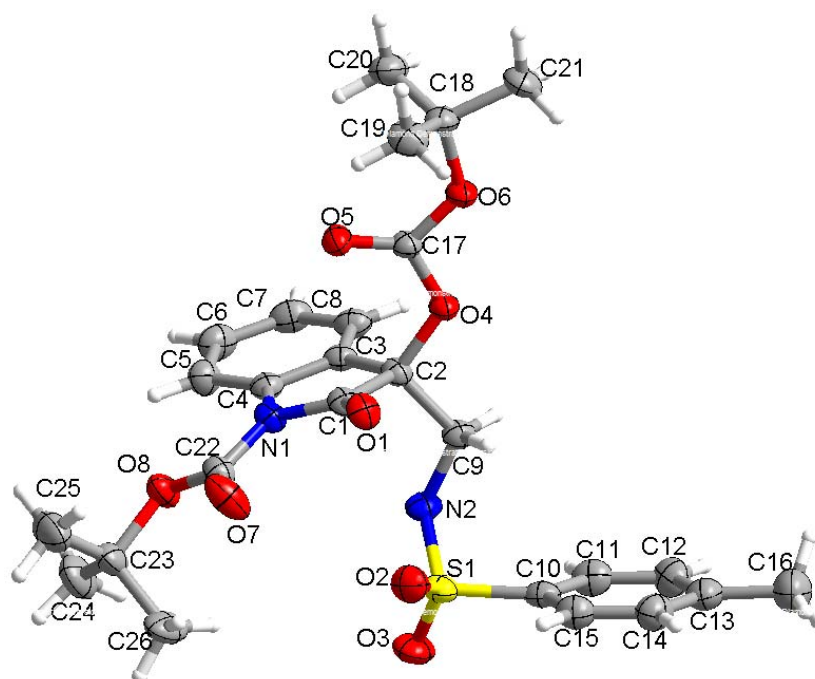
Absolute configurations of **3a-p**, **3r** and **7** are determined by *X*-ray structure analysis of the product **3q**.



**Fig. S3** Absolute configuration of **3q** (CCDC 1836991).

*Displacement ellipsoids are drawn at the 30% probability level. (Solvent: EA:PE = 1:10)*

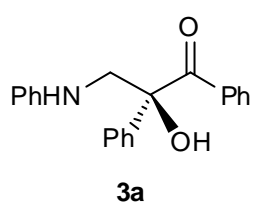
Absolute configurations of **5a-l** are determined by *X*-ray structure analysis of the product **9**.



**Fig. S4** Absolute configuration of **11** (CCDC 1843336).

*Displacement ellipsoids are drawn at the 30% probability level. (Solvent: dichloromethane)*

## 7. Characterization of adducts

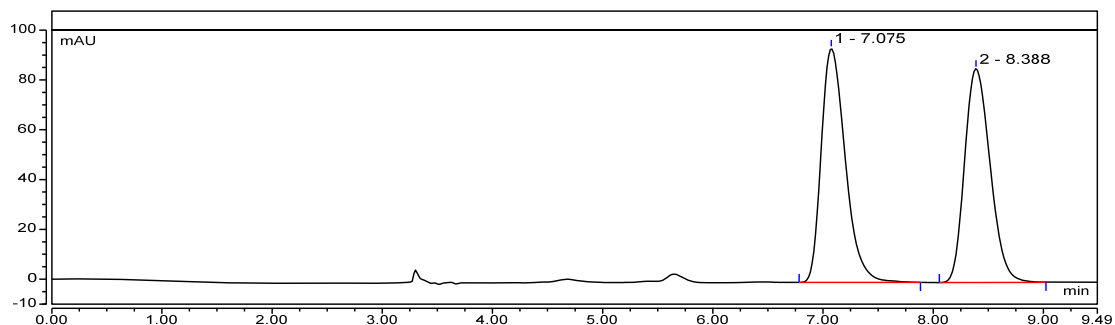


Yellow oil; 27.0 mg, 85% yield; 93% ee;  $[\alpha]_D^{22} +195.8$  (*c* 2.0, CHCl<sub>3</sub>);

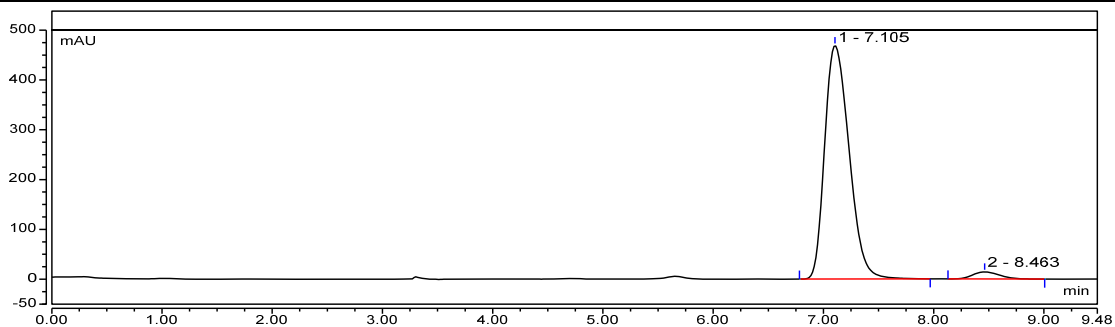
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, *J* = 7.4 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.13 (m, 6H), 7.06 (t, *J* = 7.9 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 2H), 4.54 (s, 1H), 4.05 (d, *J* = 12.9

Hz, 1H), 3.42 (d, *J* = 12.9 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  200.7, 148.3, 140.2, 134.5, 133.0, 130.6, 129.4, 129.2, 128.4, 128.3, 125.2, 119.2, 114.6, 82.4, 53.7; HRMS (ESI) *m/z* 318.1489 (M+H<sup>+</sup>), calc. for C<sub>21</sub>H<sub>20</sub>N<sub>1</sub>O<sub>2</sub> 318.1494.

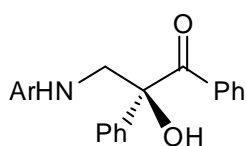
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.1 min (major) and 8.5 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.075	23.8053	93.94	50.81
2	8.388	23.0462	85.84	49.19



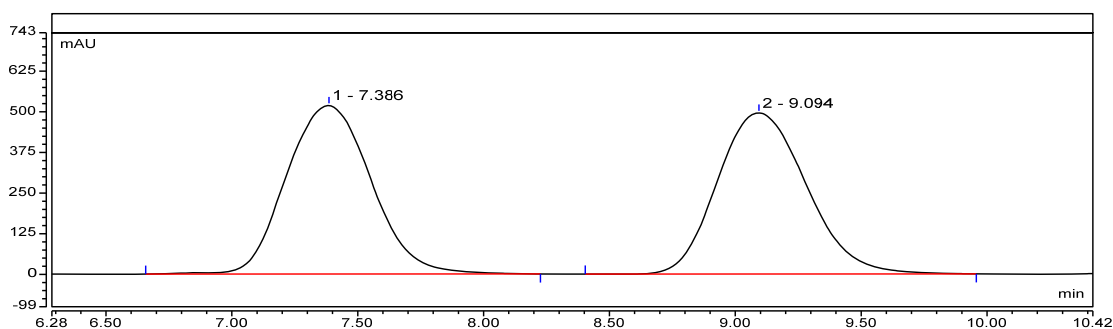
Entry	Retention Time	Area	Height	%Area
1	7.105	120.5333	468.63	96.78
2	8.463	4.0084	14.23	3.22



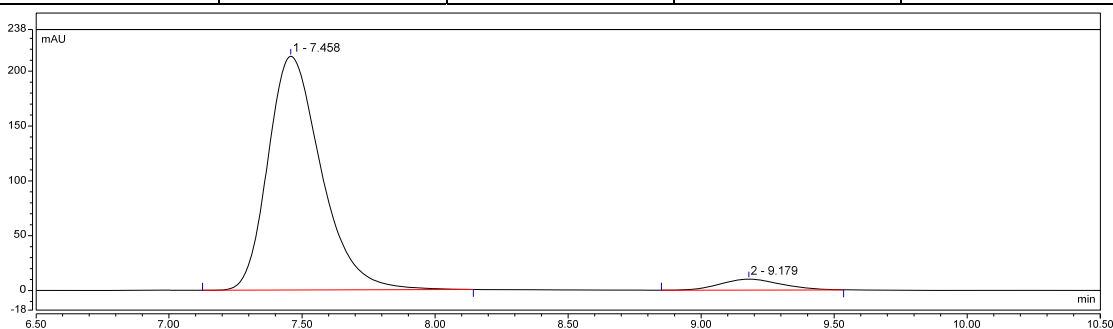
Yellow solid; Mp 74.7 – 75.2 °C; 29.2 mg, 83% yield; 90% ee;  $[\alpha]_D^{22}$  +140.4 (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.16 (m, 6H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 4.49 (s, 1H), 4.02 (d, *J* = 12.8 Hz, 1H), 3.41 (d, *J* = 12.8 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.6, 146.8, 139.9, 134.2, 133.1, 130.5, 129.2, 128.5, 128.3, 125.2, 123.7, 115.6, 82.2, 53.6; HRMS (ESI) *m/z* 352.1113 (M+H<sup>+</sup>), calc. for C<sub>21</sub>H<sub>19</sub>N<sub>1</sub>O<sub>2</sub>Cl<sub>1</sub> 352.1104.

**3b**: Ar = 4-ClPh

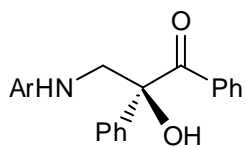
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.5 min (major) and 9.2 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.386	202.8690	518.39	49.98
2	9.094	203.0450	495.29	50.02



Entry	Retention Time	Area	Height	%Area
1	7.458	49.3688	213.11	94.99
2	9.179	2.6047	9.92	5.01



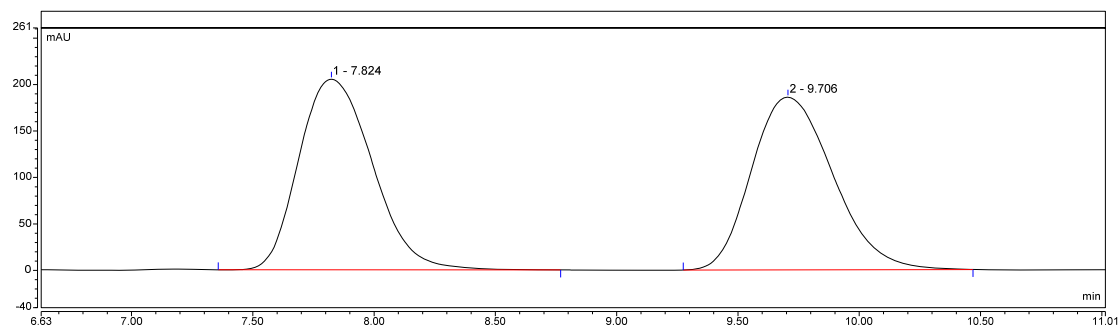
Yellow solid; Mp 74.5 – 75.7 °C; 33.7 mg, 85% yield; 91% ee;  $[\alpha]_D^{22}$  +137.7 (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.20 (m, 8H), 6.55 (d, *J* = 8.8 Hz, 2H), 4.57 (s, 1H), 4.11 (d, *J* = 12.8 Hz, 1H), 3.51 (d, *J* = 12.8 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.6, 147.2, 139.8, 134.2, 133.1, 132.1, 130.5, 129.2,

**3c**: Ar = 4-BrPh

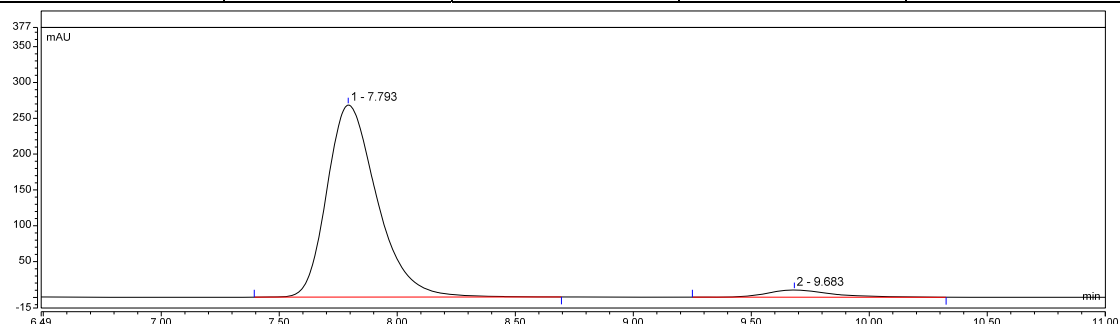


128.5, 128.3, 125.2, 116.0, 110.8, 82.2, 53.4; HRMS (ESI)  $m/z$  396.0598 ( $M+H^+$ ), calc. for  $C_{21}H_{19}N_1O_2Br_1$  396.0599.

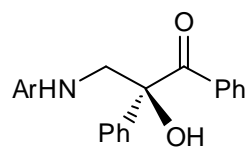
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.8 min (major) and 9.7 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.824	72.2412	205.21	49.92
2	9.706	72.4748	185.87	50.08



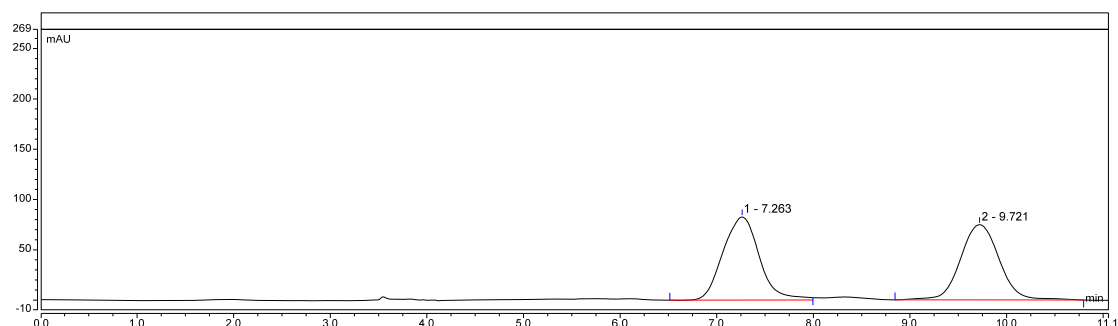
Entry	Retention Time	Area	Height	%Area
1	7.793	65.9559	267.97	95.47
2	9.683	3.1275	10.06	4.53



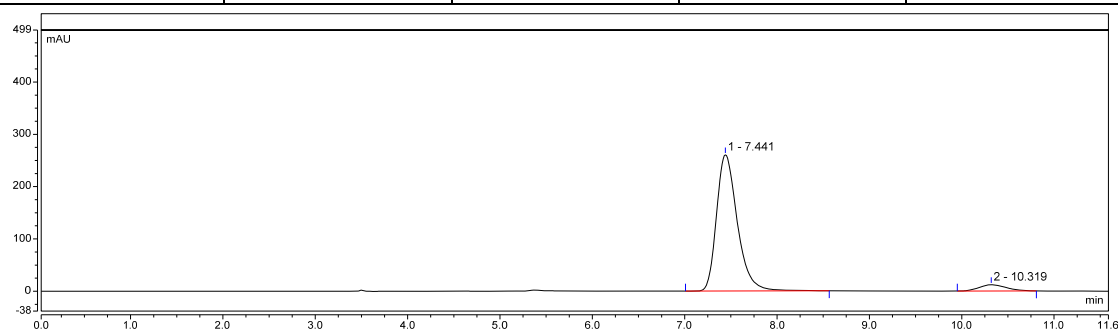
**3d:** Ar = 3-ClPh

Yellow oil; 31.3 mg, 89% yield; 90% ee;  $[\alpha]_D^{22} +120.3$  ( $c$  2.0,  $CHCl_3$ );  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.74 (d,  $J$  = 7.4 Hz, 2H), 7.45 (d,  $J$  = 7.1 Hz, 2H), 7.41 – 7.15 (m, 6H), 6.95 (t,  $J$  = 8.0 Hz, 1H), 6.62 (d,  $J$  = 7.9 Hz, 1H), 6.54 (d,  $J$  = 1.9 Hz, 1H), 6.44 (dd,  $J$  = 8.2, 1.6 Hz, 1H), 4.45 (s, 1H), 4.03 (m, 2H), 3.45 (d,  $J$  = 12.8 Hz, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  200.5, 149.4, 139.8, 135.1, 134.2, 133.2, 130.4, 130.3, 129.2, 128.6, 128.3, 125.3, 118.9, 114.0, 112.8, 82.2, 53.0; HRMS (ESI)  $m/z$  352.1098 ( $M+H^+$ ), calc. for  $C_{21}H_{19}N_1O_2Cl_1$  352.1104.

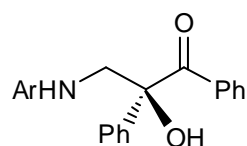
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.4 min (major) and 10.3 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.263	36.0975	82.57	50.97
2	9.721	34.7255	74.73	49.03



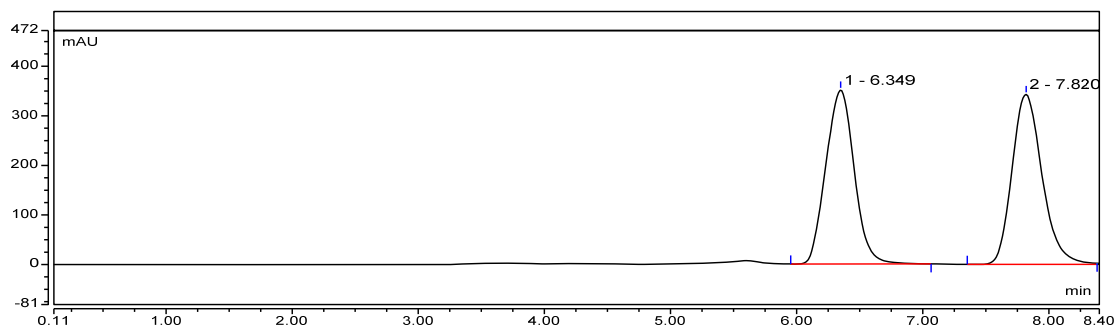
Entry	Retention Time	Area	Height	%Area
1	7.441	68.0407	260.49	94.88
2	10.319	3.6742	11.66	5.12



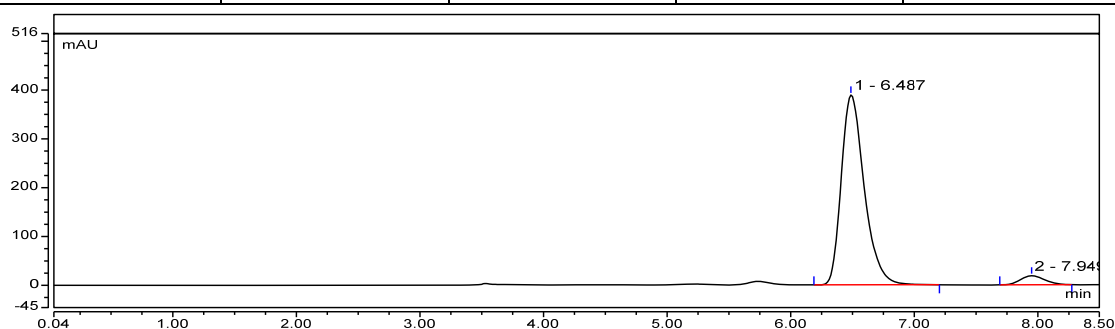
**3e:** Ar = 4-MePh

Yellow oil; 28.2 mg, 85% yield; 91% ee;  $[\alpha]_D^{22} +94.2$  (c 2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 7.5$  Hz, 2H), 7.46 (d,  $J = 7.3$  Hz, 2H), 7.33 (m, 3H), 7.19 (m, 3H), 6.88 (d,  $J = 8.1$  Hz, 2H), 6.53 (d,  $J = 8.3$  Hz, 2H), 4.62 (s, 1H), 4.03 (d,  $J = 12.7$  Hz, 1H), 3.35 (d,  $J = 12.7$  Hz, 1H), 2.14 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.6, 145.7, 140.1, 134.3, 132.9, 130.5, 129.8, 129.0, 128.6, 128.3, 128.1, 125.0, 114.9, 82.1, 54.3, 20.5; HRMS (ESI)  $m/z$  332.1660 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{22}\text{N}_1\text{O}_2$  332.1651.

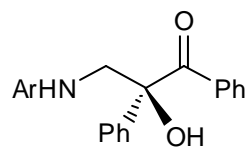
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 6.5 min (major) and 7.9 min (minor).



Entry	Retention Time	Area	Height	%Area
1	6.349	91.4757	350.96	49.09
2	7.820	94.8612	342.96	50.91



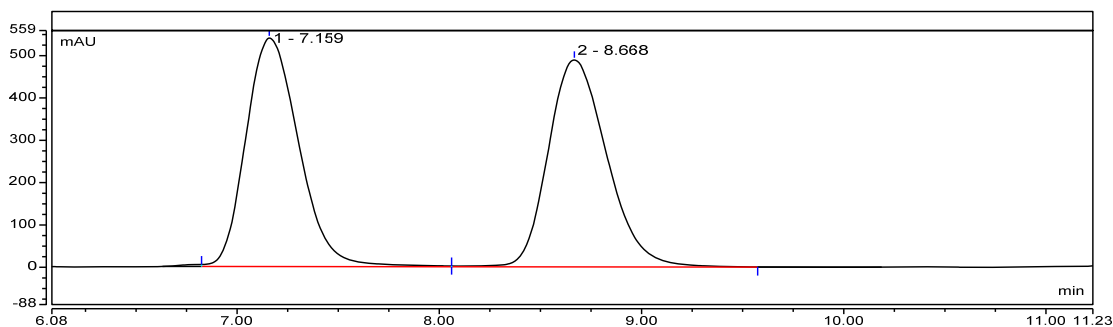
Entry	Retention Time	Area	Height	%Area
1	6.487	83.8961	388.80	95.45
2	7.949	4.0032	18.08	4.55



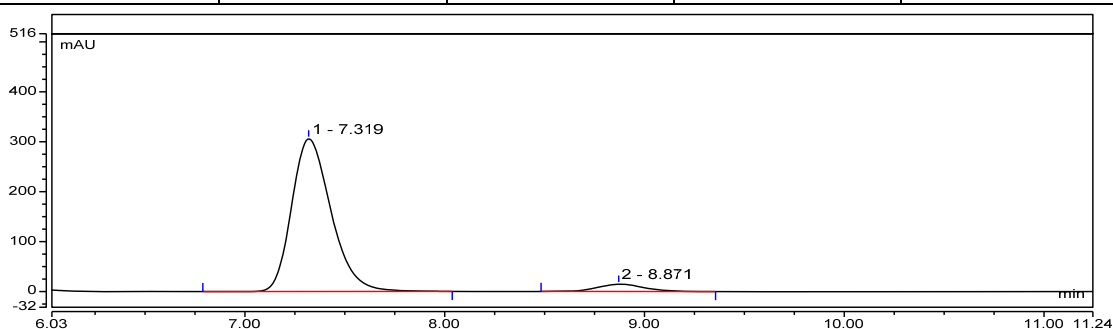
**3f:** Ar = 3-MePh

Yellow solid; Mp 73.0 – 74.6 °C; 25.8 mg, 78% yield; 90% ee;  $[\alpha]_D^{22}$  +83.2 (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.27 (m, 6H), 7.06 (m, 1H), 6.61 (d, *J* = 7.4 Hz, 1H), 6.52 (s, 2H), 4.63 (s, 1H), 4.14 (d, *J* = 12.8 Hz, 1H), 3.51 (d, *J* = 12.8 Hz, 1H), 2.26 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.6, 148.2, 140.2, 139.3, 134.4, 33.0, 130.6, 129.3, 129.1, 128.4, 128.2, 125.2, 120.1, 115.4, 111.8, 82.2, 53.8, 21.7; HRMS (ESI) *m/z* 332.1652 (M+H<sup>+</sup>), calc. for C<sub>22</sub>H<sub>22</sub>N<sub>1</sub>O<sub>2</sub> 332.1651.

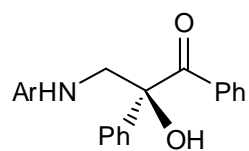
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.3 min (major) and 8.9 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.159	163.8425	539.85	49.93
2	8.668	164.2897	488.66	50.07



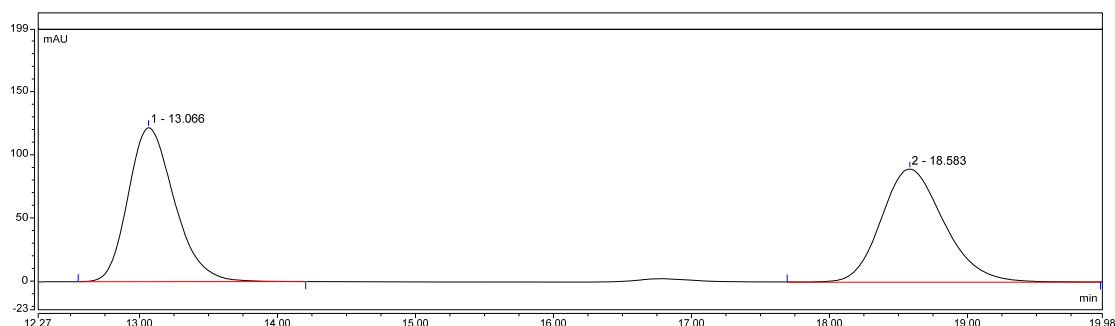
Entry	Retention Time	Area	Height	%Area
1	7.319	69.7140	305.77	94.97
2	8.871	3.6911	14.32	5.03



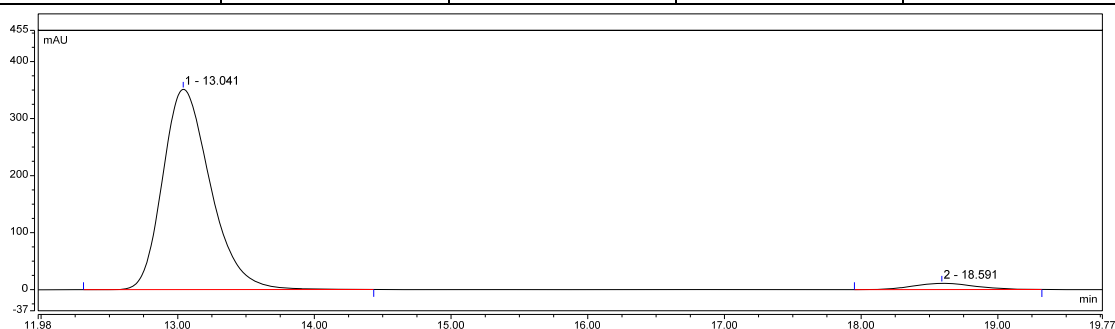
**3g**: Ar = 4-OMePh

Yellow oil; 29.5 mg, 85% yield; 92% ee;  $[\alpha]_D^{22} +36.2$  (*c* 2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.6$  Hz, 2H), 7.56 (d,  $J = 7.3$  Hz, 2H), 7.34 (m, 6H), 6.71 (dd,  $J = 27.5, 8.9$  Hz, 4H), 4.79 (s, 1H), 4.12 (d,  $J = 12.6$  Hz, 1H), 3.74 (s, 3H), 3.38 (d,  $J = 12.6$  Hz, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.6, 153.4, 142.1, 140.3, 134.4, 133.0, 130.6, 129.1, 128.3, 128.2, 125.1, 116.4, 114.9, 82.1, 55.8, 55.3; HRMS (ESI)  $m/z$  348.1614 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{22}\text{N}_1\text{O}_3$  348.1600.

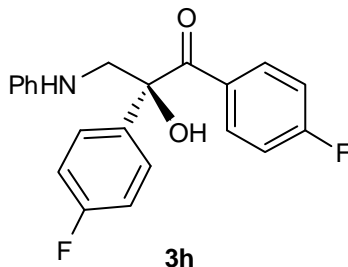
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 13.0 min (major) and 18.6 min (minor).



Entry	Retention Time	Area	Height	%Area
1	13.066	47.3003	121.84	49.94
2	18.583	47.4123	89.47	50.06



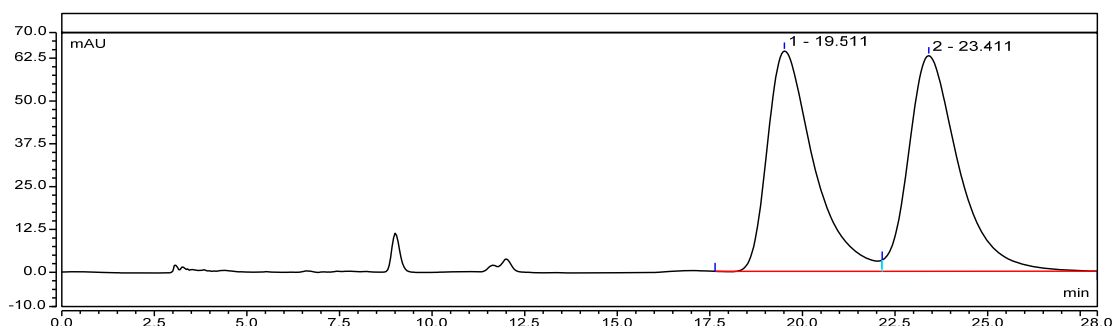
Entry	Retention Time	Area	Height	%Area
1	13.041	142.1831	351.23	96.10
2	18.591	5.7710	11.04	3.90



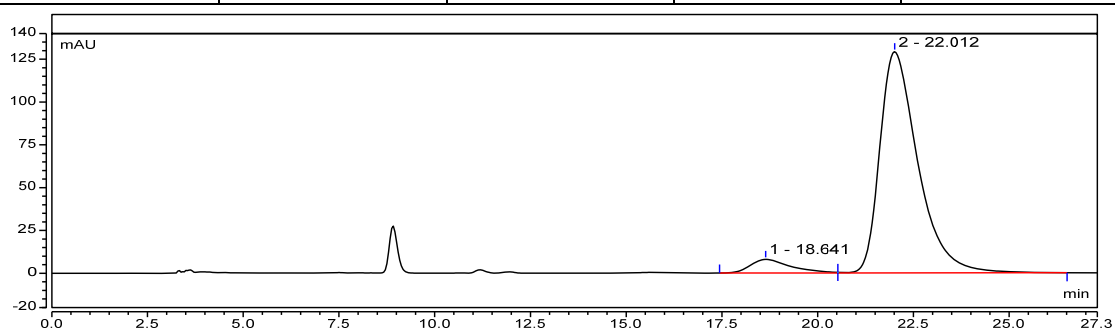
Yellow oil; 24.4 mg, 69% yield; 88% ee;  $[\alpha]_D^{22} +62.8$  (c 2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (m, 2H), 7.53 (m, 2H), 7.19 (t,  $J = 7.8$  Hz, 2H), 7.10 (t,  $J = 8.6$  Hz, 2H), 6.99 (t,  $J = 8.6$  Hz, 2H), 6.80 (t,  $J = 7.3$  Hz, 1H), 6.72 (d,  $J = 8.0$  Hz, 2H), 4.58 (s, 1H), 4.12 (d,  $J = 13.0$  Hz, 1H), 3.40 (d,  $J = 13.0$

Hz, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.6, 167.3, 164.3, 163.9, 161.1, 148.1, 135.8, 135.7, 133.6, 135.5, 130.5, 130.4, 129.5, 126.8, 126.7, 119.5, 116.3, 116.0, 115.6, 115.3, 114.7, 82.0, 54.3; HRMS (ESI)  $m/z$  354.1308 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{21}\text{H}_{18}\text{N}_1\text{O}_2\text{F}_2$  354.1306.

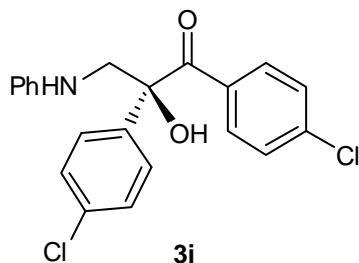
The ee was determined by HPLC analysis: CHIRALPAK cellulose-3 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.6 min (minor) and 22.0 min (major).



Entry	Retention Time	Area	Height	%Area
1	19.511	93.4565	64.37	48.98
2	23.411	97.3659	62.88	51.02



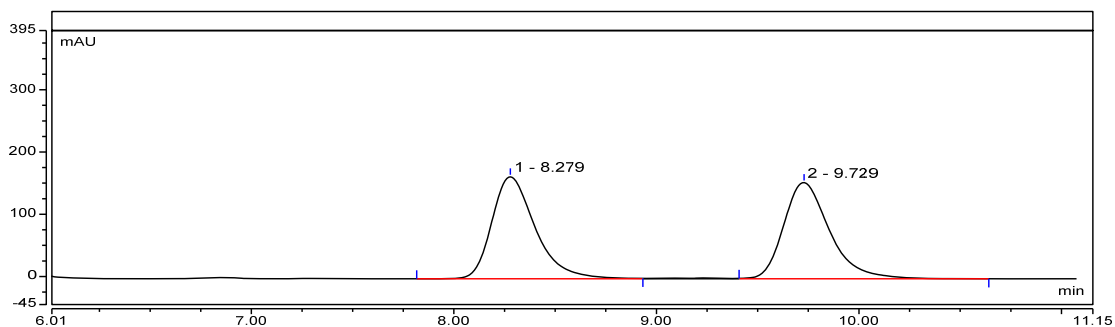
Entry	Retention Time	Area	Height	%Area
1	18.641	9.6307	7.93	6.08
2	22.012	148.6794	129.21	93.92



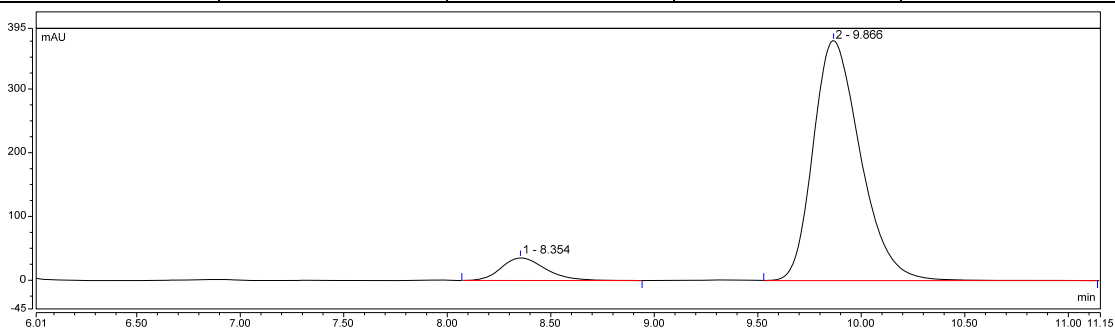
Yellow oil; 27.8 mg, 72% yield; 84% ee;  $[\alpha]_D^{22} +157.9$  (c 2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.6$  Hz, 2H), 7.40 (d,  $J = 8.6$  Hz, 2H), 7.30 (d,  $J = 8.6$  Hz, 2H), 7.20 (m, 2H), 7.11 (t,  $J = 7.9$  Hz, 2H), 6.73 (t,  $J = 7.3$  Hz, 1H), 6.64 (d,  $J = 7.9$  Hz, 2H), 4.47 (s, 1H), 4.03 (d,  $J = 13.1$  Hz,

1H), 3.29 (d,  $J = 13.1$  Hz, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 148.0, 139.7, 138.4, 134.5, 132.4, 132.2, 129.5, 129.4, 128.6, 126.3, 119.6, 114.8, 82.1, 54.2; HRMS (ESI)  $m/z$  386.0719 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{21}\text{H}_{18}\text{N}_1\text{O}_2\text{Cl}_2$  386.0715.

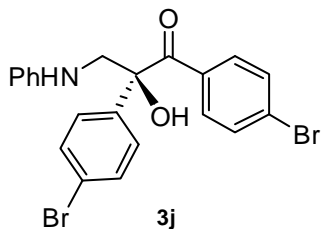
The ee was determined by HPLC analysis: CHIRALPAK IB (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.4 min (minor) and 9.9 min (major).



Entry	Retention Time	Area	Height	%Area
1	8.279	40.7934	163.78	50.13
2	9.729	40.5842	154.52	49.87

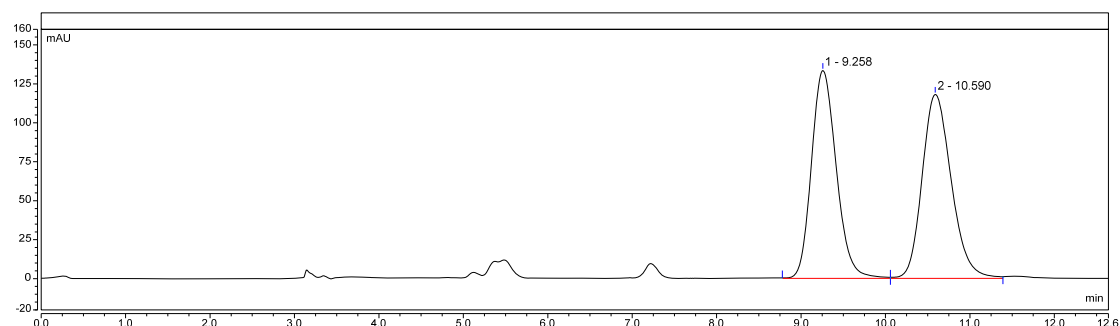


Entry	Retention Time	Area	Height	%Area
1	8.354	8.6818	35.45	8.02
2	9.866	99.5794	376.29	91.98

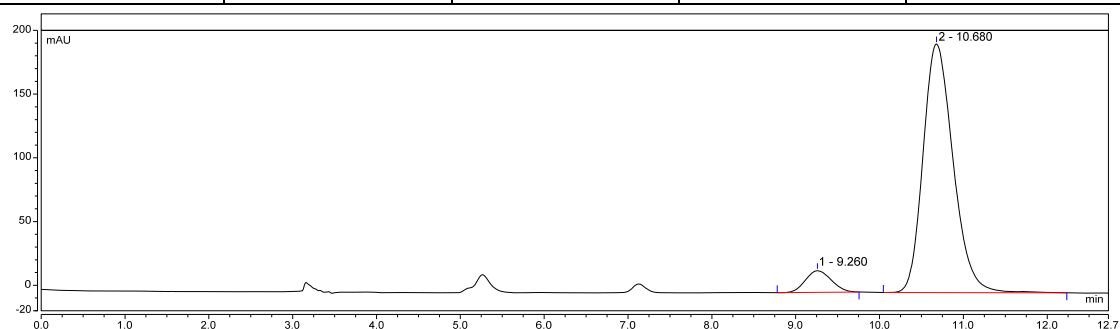


Yellow oil; 36.1 mg, 76% yield; 86% ee;  $[\alpha]_D^{22} +86.4$  (c 2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.6$  Hz, 2H), 7.54 (d,  $J = 8.6$  Hz, 2H), 7.44 (m, 4H), 7.19 (t,  $J = 7.9$  Hz, 2H), 6.81 (t,  $J = 7.3$  Hz, 1H), 6.72 (d,  $J = 7.8$  Hz, 2H), 4.53 (s, 1H), 4.11 (d,  $J = 13.1$  Hz, 1H), 3.36 (d,  $J = 13.1$  Hz, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1, 148.1, 139.0, 132.9, 132.5, 132.3, 131.7, 129.6, 128.7, 126.7, 122.8, 119.8, 114.9, 82.3, 54.3.

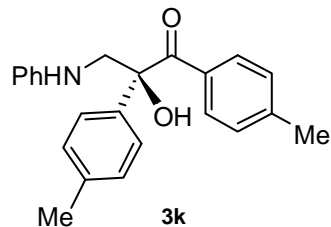
The ee was determined by HPLC analysis: CHIRALPAK cellulose-4 (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.3 min (minor) and 10.7 min (major) ; HRMS (ESI)  $m/z$  473.9696 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{21}\text{H}_{18}\text{N}_1\text{O}_2\text{Br}_2$  473.9704.



Entry	Retention Time	Area	Height	%Area
1	9.258	45.3990	133.40	49.04
2	10.590	47.1722	118.03	50.96



Entry	Retention Time	Area	Height	%Area
1	9.260	6.1037	17.07	7.00
2	10.680	81.1539	195.05	93.00



Yellow solid; Mp 71.4 – 72.5 °C; 28.0 mg, 81% yield; 93% ee;

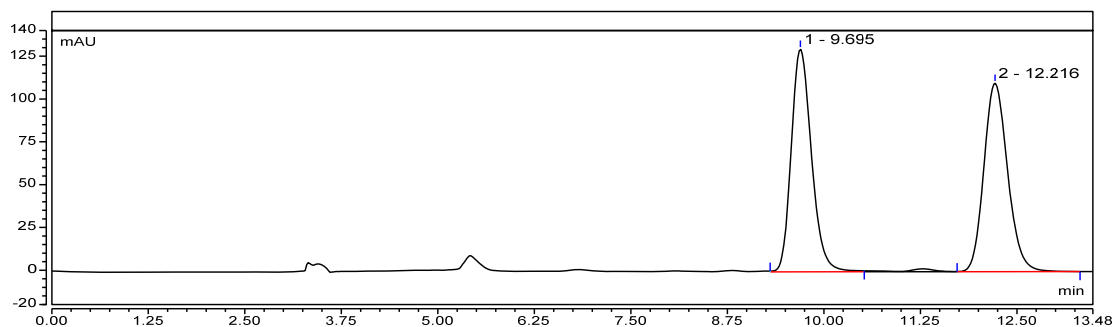
$[\alpha]_D^{22} +156.7$  (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.10

(m, 6H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 2H), 4.68

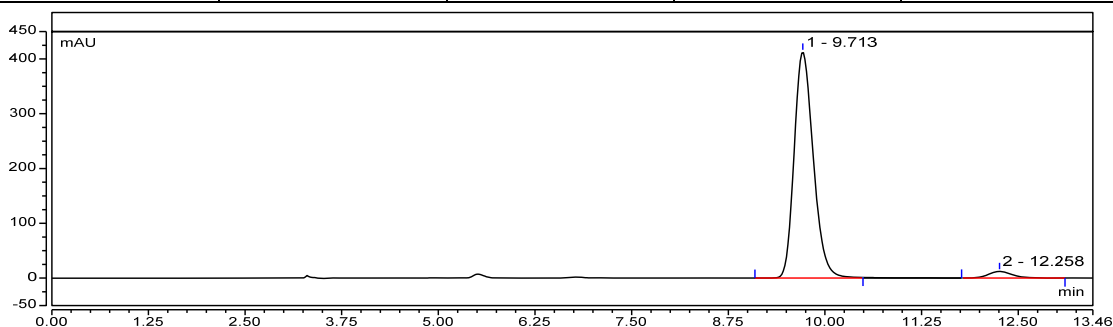
(s, 1H), 4.13 (d, *J* = 12.7 Hz, 1H), 3.55 (d, *J* = 12.7 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.2, 148.3, 143.9, 138.1, 137.4, 131.7, 130.7, 129.8, 129.4, 128.9, 125.1, 119.0, 114.5, 82.0, 53.6, 21.7, 21.3; HRMS (ESI) *m/z* 346.1808 (M+H<sup>+</sup>), calc. for C<sub>23</sub>H<sub>24</sub>N<sub>1</sub>O<sub>2</sub> 346.1807.

The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 9.7 min (major) and 12.3 min (minor).

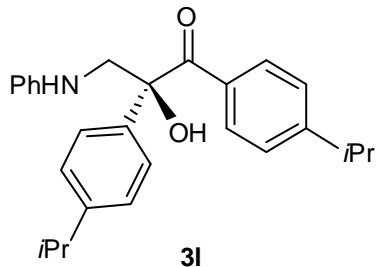




Entry	Retention Time	Area	Height	%Area
1	9.695	39.5473	130.10	50.21
2	12.216	39.2218	110.10	49.79

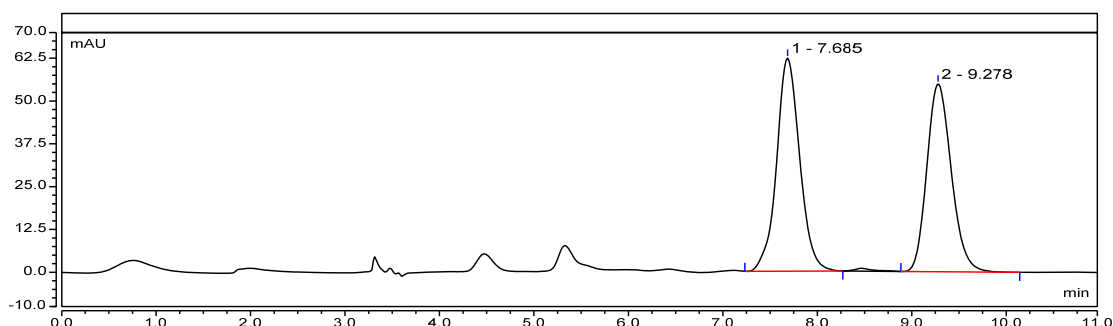


Entry	Retention Time	Area	Height	%Area
1	9.713	119.2228	412.78	96.52
2	12.258	4.3016	4.3016	3.48

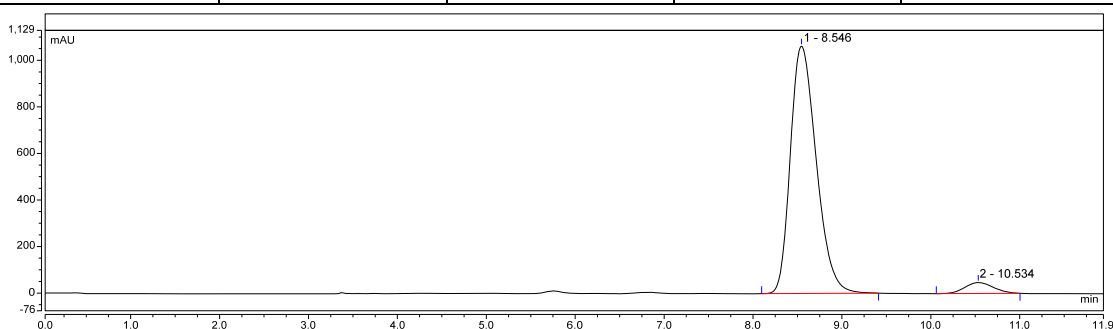


Yellow oil; 33.3 mg, 83% yield; 91% ee;  $[\alpha]_D^{22} +201.6$  (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 4.6 Hz, 2H), 7.13 (t, *J* = 8.8 Hz, 4H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 4.64 (s, 1H), 4.10 (d, *J* = 12.7 Hz, 1H), 3.54 (d, *J* = 12.7 Hz, 1H), 2.98 – 2.77 (m, 2H), 1.24 (d, 6H), 1.19(d, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.4, 154.6, 149.1, 148.4, 137.7, 132.1, 131.0, 129.4, 127.3, 126.5, 125.3, 119.0, 114.5, 53.5, 34.4, 34.0, 24.1, 23.8, 23.8; HRMS (ESI) *m/z* 402.2427 (M+H<sup>+</sup>), calc. for C<sub>27</sub>H<sub>32</sub>N<sub>1</sub>O<sub>2</sub> 402.2433.

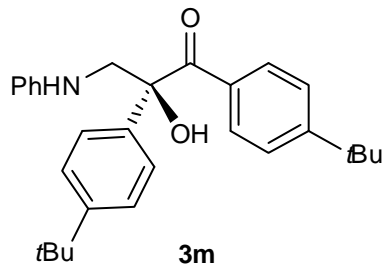
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.5 min (major) and 10.5 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.685	17.6257	62.24	51.75
2	9.278	16.4313	54.85	48.25

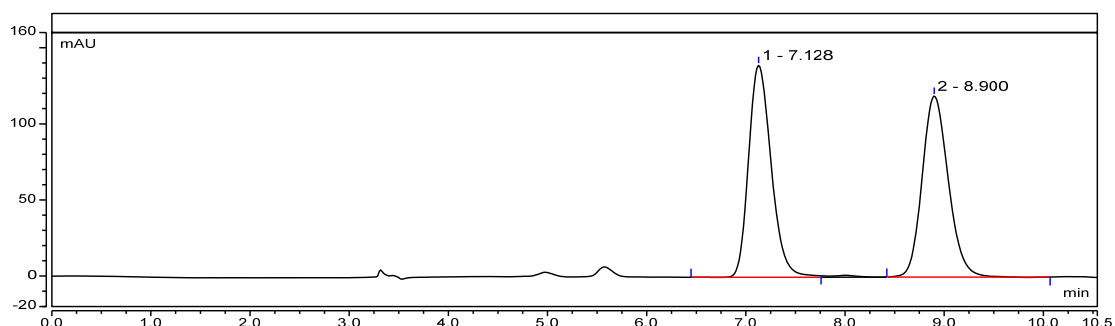


Entry	Retention Time	Area	Height	%Area
1	8.546	358.6272	1062.45	95.36
2	10.534	17.4492	47.06	4.64

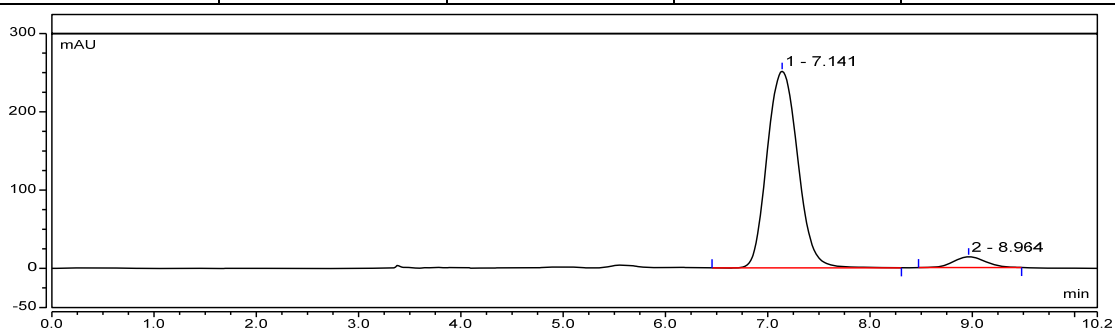


Yellow solid; Mp 57.7 – 58.5 °C; 36.5 mg, 85% yield; 90% ee;  $[\alpha]_D^{22} +89.6$  (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 0H), 6.67 (d, *J* = 7.9 Hz, 1H), 4.66 (s, 0H), 4.12 (d, *J* = 12.7 Hz, 1H), 3.58 (d, *J* = 12.7 Hz, 1H), 1.33 (s, 3H), 1.28 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.5, 156.9, 151.4, 148.4, 137.3, 131.7, 130.7, 129.4, 126.2, 125.4, 125., 119.0, 114.6, 82.1, 53.5, 35.3, 34.8, 31.5, 31.2; HRMS (ESI) *m/z* 430.2754 (M+H<sup>+</sup>), calc. for C<sub>29</sub>H<sub>36</sub>N<sub>1</sub>O<sub>2</sub> 430.2746.

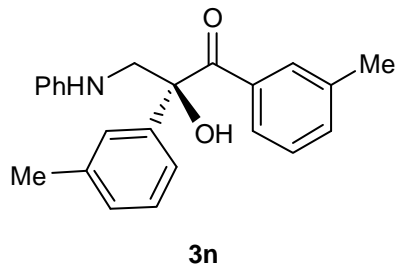
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.1 min (major) and 9.0 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.128	36.7559	139.24	50.26
2	8.900	36.3705	118.97	49.74

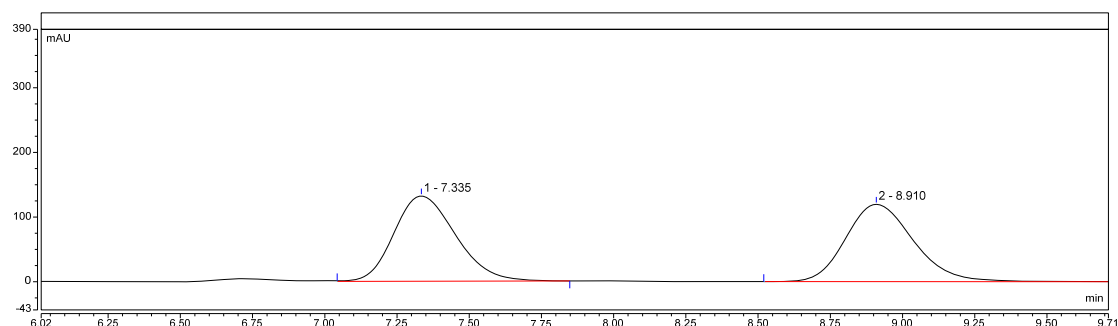


Entry	Retention Time	Area	Height	%Area
1	7.141	86.6588	250.77	94.91
2	8.964	4.6521	13.34	5.09

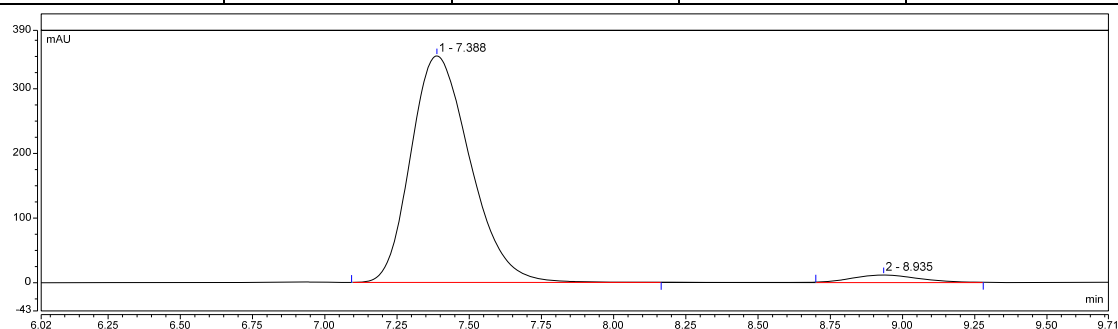


Yellow oil; 28.0 mg, 81% yield; 93% ee;  $[\alpha]_D^{22} +124.8$  ( $c$  2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (s, 1H), 7.51 (d,  $J = 7.7$  Hz, 1H), 7.19 (m, 3H), 7.12 (s, 1H), 7.04 (t,  $J = 7.8$  Hz, 4H), 6.64 (t,  $J = 7.3$  Hz, 1H), 6.57 (d,  $J = 7.8$  Hz, 2H), 4.50 (s, 1H), 4.01 (d,  $J = 12.7$  Hz, 1H), 3.40 (d,  $J = 12.8$  Hz, 1H), 2.24 (s, 3H), 2.18 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  201.0, 148.2, 140.1, 138.9, 138.0, 134.4, 133.8, 130.8, 129.4, 129.2, 129.0, 127.8, 127.8, 125.8, 122.2, 119.1, 114.6, 82.3, 53.6, 21.7, 21.5; HRMS (ESI)  $m/z$  346.1810 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{23}\text{H}_{24}\text{N}_1\text{O}_2$  318.1494.

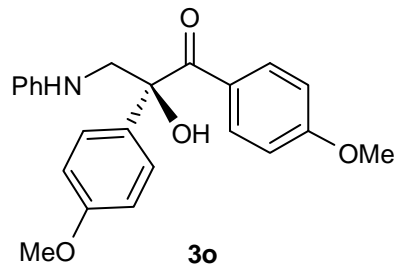
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 7.4 min (major) and 8.9 min (minor).



Entry	Retention Time	Area	Height	%Area
1	7.335	32.5326	131.69	50.03
2	8.910	32.4971	119.48	49.97

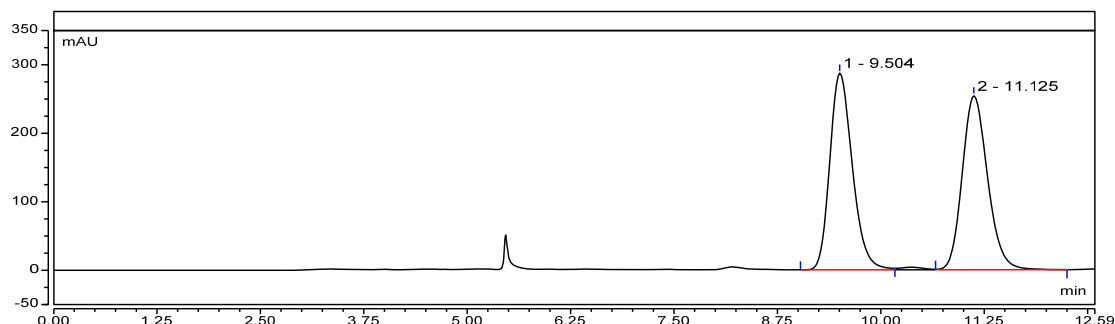


Entry	Retention Time	Area	Height	%Area
1	7.388	83.5608	350.26	96.40
2	8.935	3.1171	11.64	3.60

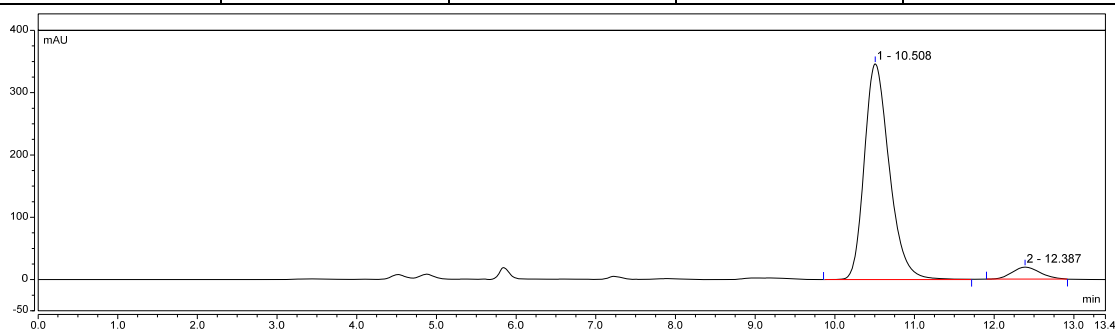


Yellow solid; Mp 77.6 – 78.9 °C; 31.3 mg, 83% yield; 88% ee;  $[\alpha]_D^{22} +21.9$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.77 (m, 3H), 6.69 (d, *J* = 7.9 Hz, 2H), 4.69 (s, 1H), 4.07 (d, *J* = 12.6 Hz, 1H), 3.80 (s, 3H), 3.79(s, 3H), 3.53 (d, *J* = 12.6 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 199.0, 163.4, 159.5, 148.3, 133.1, 132.7, 129.4, 126.9, 126.5, 118.9, 114.5, 114.4, 113.5, 81.5, 55.5, 55.4, 53.6; HRMS (ESI) *m/z* 378.1700 (M+H<sup>+</sup>), calc. for C<sub>23</sub>H<sub>24</sub>N<sub>1</sub>O<sub>4</sub> 378.1705.

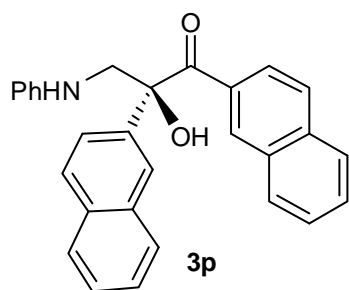
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.5 min (major) and 12.4 min (minor).



Entry	Retention Time	Area	Height	%Area
1	9.504	90.7926	287.30	50.12
2	11.125	90.3408	254.01	49.88



Entry	Retention Time	Area	Height	%Area
1	10.508	125.8121	346.24	94.20
2	12.387	7.7515	19.15	5.80

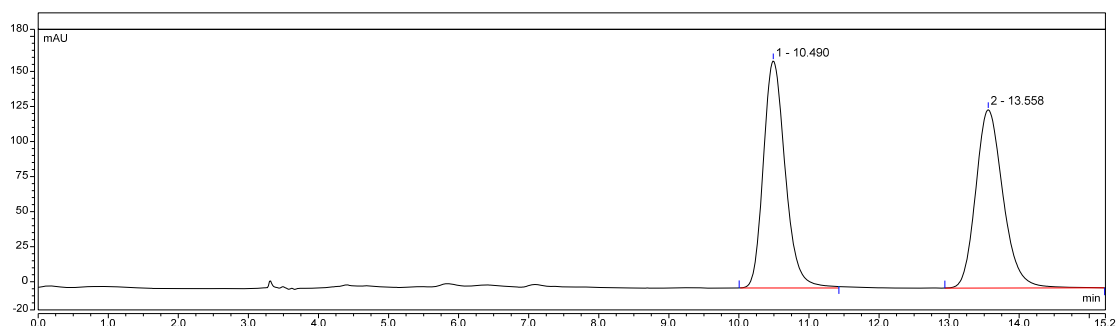


Yellow solid; Mp 52.8 – 53.6 °C; 25.5 mg, 61% yield; 91% ee;

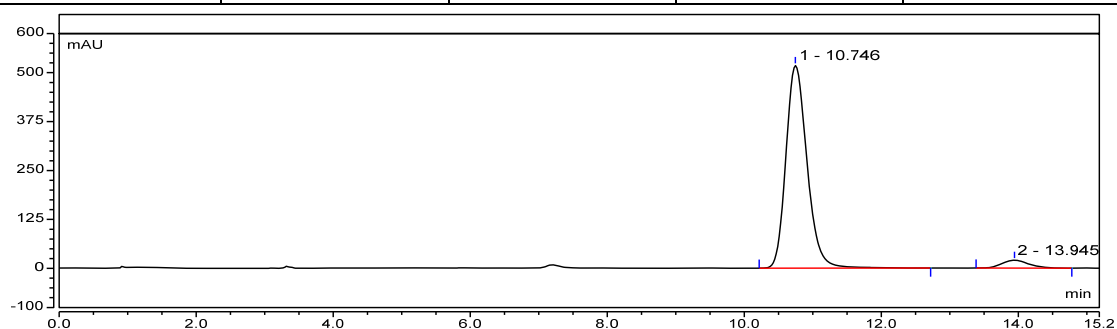
$[\alpha]_D^{22} +47.3$  (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.55 (s, 1H), 8.14 (s, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.93 – 7.81 (m, 3H), 7.80 – 7.66 (m, 4H), 7.57 – 7.40 (m, 4H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.78 (m, 3H), 4.80 (s, 1H), 4.31 (d, *J* =

12.9 Hz, 1H), 3.63 (d, *J* = 12.8 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 200.4, 148.3, 137.8, 135.4, 133.5, 133.2, 133.0, 132.2, 131.6, 123.0, 129.5, 129.1, 128.7, 128.4, 127.9, 127.8, 127.7, 126.6, 126.5, 125.9, 124.3, 122.8, 119.3, 114.68 (s, 6H), 82.7, 54.1; HRMS (ESI) *m/z* 418.1810 (M+H<sup>+</sup>), calc. for C<sub>29</sub>H<sub>24</sub>N<sub>1</sub>O<sub>2</sub> 418.1807.

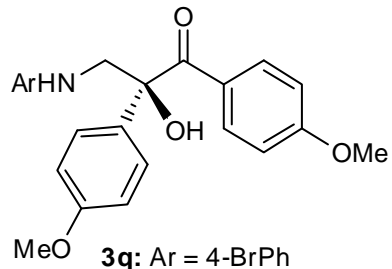
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 10.7 min (major) and 13.9 min (minor).



Entry	Retention Time	Area	Height	%Area
1	10.490	58.5250	161.89	50.54
2	13.558	57.2725	127.10	49.46

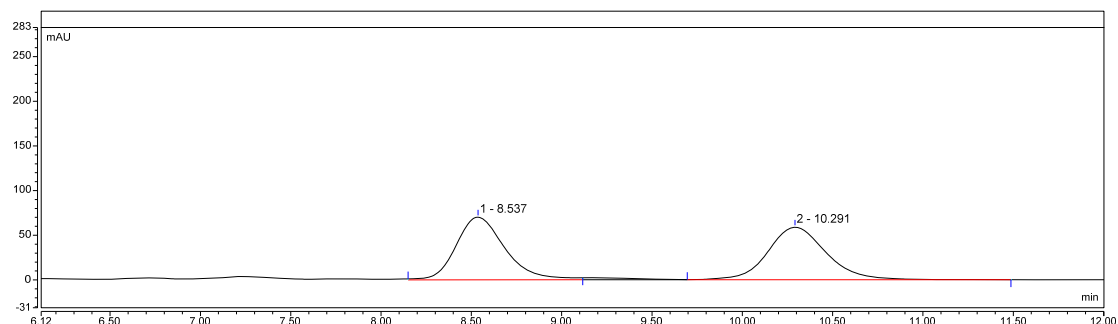


Entry	Retention Time	Area	Height	%Area
1	10.746	185.0326	517.80	95.33
2	13.945	9.0613	20.07	4.67

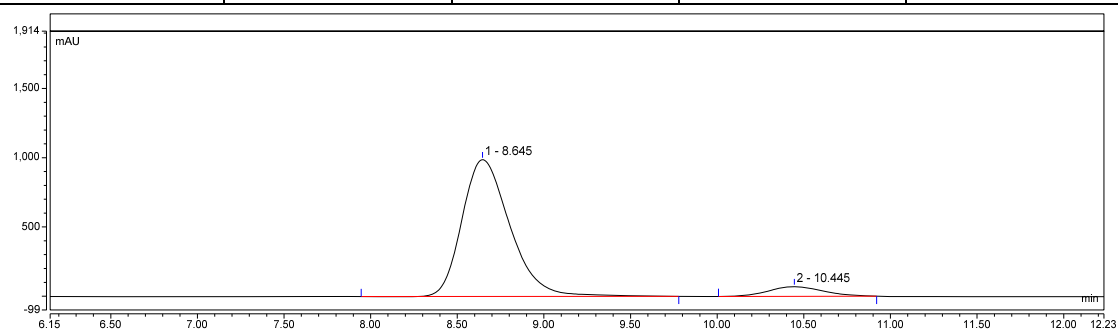


Yellow solid; Mp 108.2 – 109.5 °C; 40.6 mg, 89% yield; 97% ee;  $[\alpha]_D^{22} +53.4$  (c 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.78 (m, 2H), 7.49 – 7.36 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.53 (d, *J* = 8.7 Hz, 2H), 4.64 (s, 1H), 4.15 (s, 1H), 4.01 (d, *J* = 12.7 Hz, 1H), 3.80 (s, 6H), 3.52 (d, *J* = 12.6 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.8, 163.4, 159.5, 147.3, 133.1, 132.4, 132.0, 126.7, 126.6, 115.9, 114.5, 113.6, 110.4, 81.4, 55.5, 55.4, 53.2; HRMS (ESI) *m/z* 458.0805 (M+H<sup>+</sup>), calc. for C<sub>23</sub>H<sub>23</sub>N<sub>1</sub>O<sub>4</sub>Br<sub>1</sub> 458.0790.

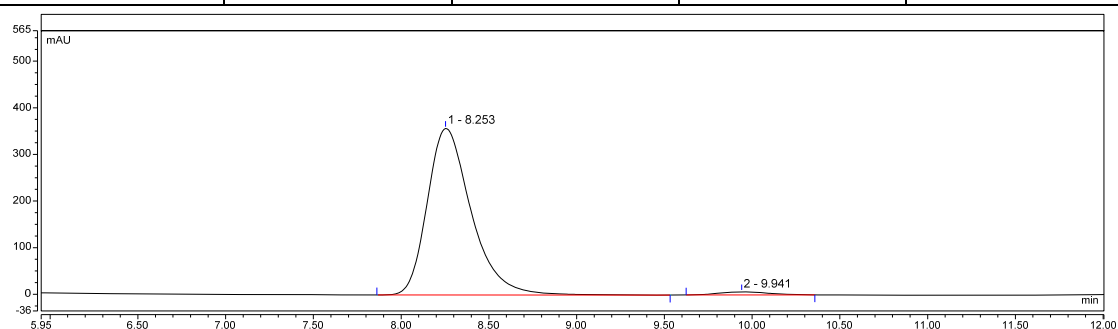
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.3 min (major) and 9.9 min (minor).



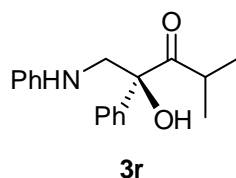
Entry	Retention Time	Area	Height	%Area
1	8.537	21.9589	70.10	49.83
2	10.291	22.1082	58.82	50.17



Entry	Retention Time	Area	Height	%Area
1	8.645	316.8719	987.56	92.56
2	10.445	25.4775	69.85	7.44

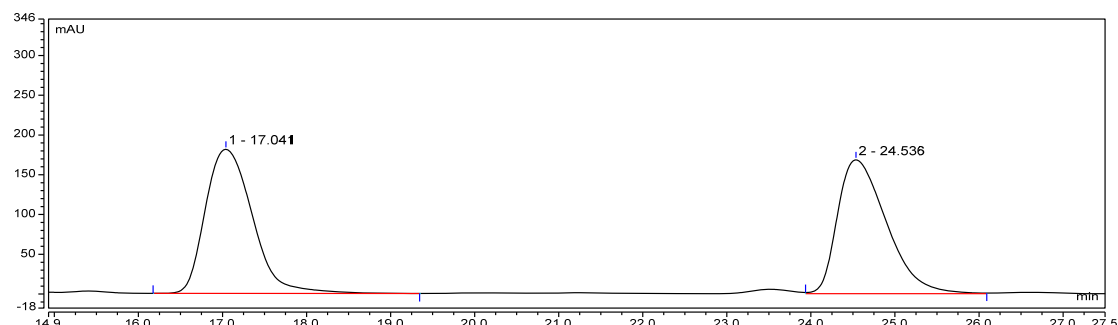


Entry	Retention Time	Area	Height	%Area
1	8.253	103.8814	357.14	98.48
2	9.941	1.6009	5.82	1.52

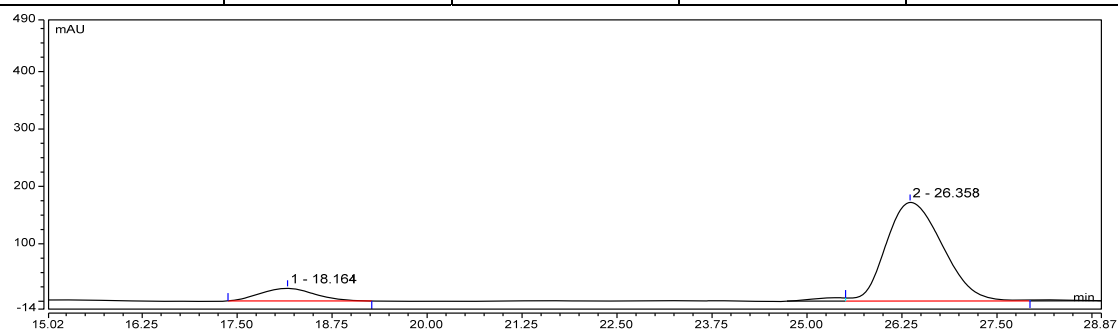


Yellow oil; 18.42 mg, 65% yield; 78% ee;  $[\alpha]_D^{22} -54.3$  (*c* 0.1,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (m, 2H), 7.44 – 7.32 (m, 3H), 7.22 (t,  $J = 7.9$  Hz, 2H), 6.80 (m, 3H), 4.86 (s, 1H), 4.16 (d,  $J = 12.2$  Hz, 1H), 3.56 (d,  $J = 12.2$  Hz, 1H), 3.08 (m, 6.7 Hz, 1H), 0.92 (d,  $J = 6.8$  Hz, 3H), 0.81 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  215.6, 147.3, 129.5, 128.9, 128.6, 125.9, 119.6, 114.8, 82.3, 50.5, 34.4, 20.5, 19.7; HRMS (ESI)  $m/z$  284.1638 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{18}\text{H}_{22}\text{NO}_2$  284.1645.

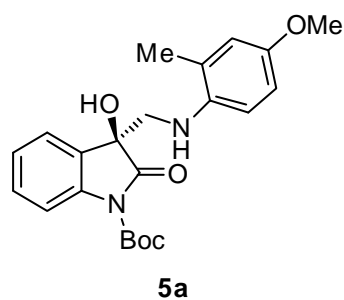
The ee was determined by HPLC analysis: CHIRALPAK IE (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 98/2; flow rate 0.5 mL/min; 25 °C; 254 nm; retention time: 18.2 min (minor) and 26.4 min (major).



Entry	Retention Time	Area	Height	%Area
1	17.041	117.7428	181.29	50.92
2	24.536	113.5090	168.34	49.08



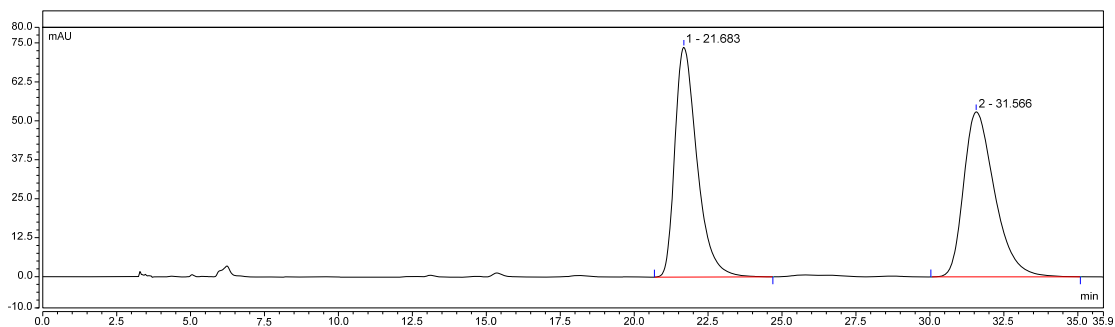
Entry	Retention Time	Area	Height	%Area
1	18.164	18.2070	22.13	10.98
2	26.354	147.5912	171.73	89.02



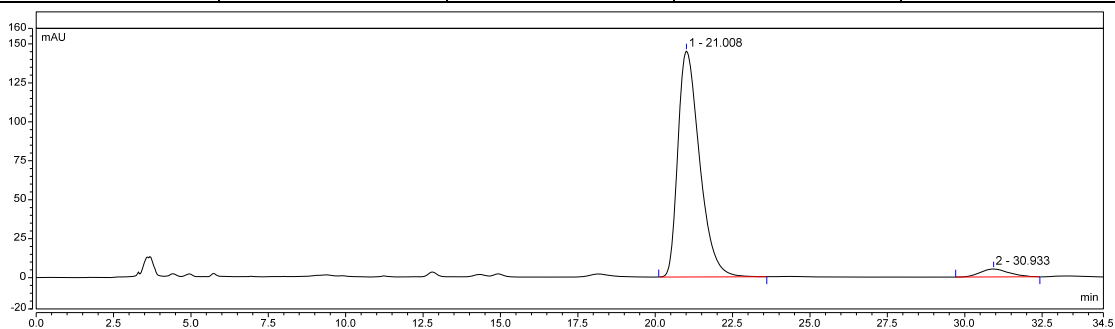
Yellow oil; 36.3 mg, 91% yield; 91% ee;  $[\alpha]_D^{22} +110.2$  (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 6.74 – 6.53 (m, 3H), 4.26 (s, 1H), 3.73 (s, 3H), 3.62 (d, *J* = 12.7 Hz, 1H), 3.34 (d, *J* = 12.6 Hz, 1H), 2.15 (s, 3H), 1.64 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.7, 152.8, 148.8, 139.7, 139.2, 130.5, 127.5, 126.1, 125.6, 124.2, 116.92, 115.42, 112.9, 111.5, 84.9, 74.3, 55.7, 52.0, 28.1, 17.8; HRMS (ESI) *m/z* 399.1926 (M+H<sup>+</sup>), calc. for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O<sub>5</sub> 399.1920.

The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 21.0 min (major) and 30.9 min (minor).

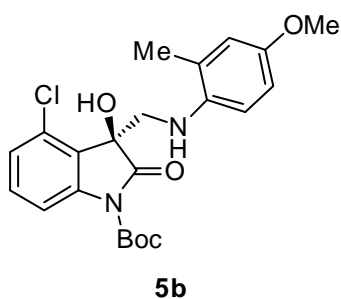




Entry	Retention Time	Area	Height	%Area
1	21.683	64.0677	73.70	49.94
2	31.566	64.2272	52.96	50.06

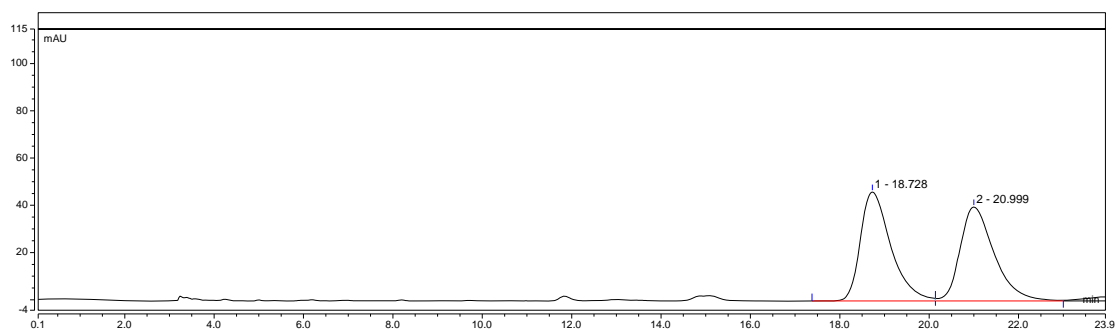


Entry	Retention Time	Area	Height	%Area
1	21.008	117.7823	144.94	95.53
2	30.933	5.5157	5.10	4.47

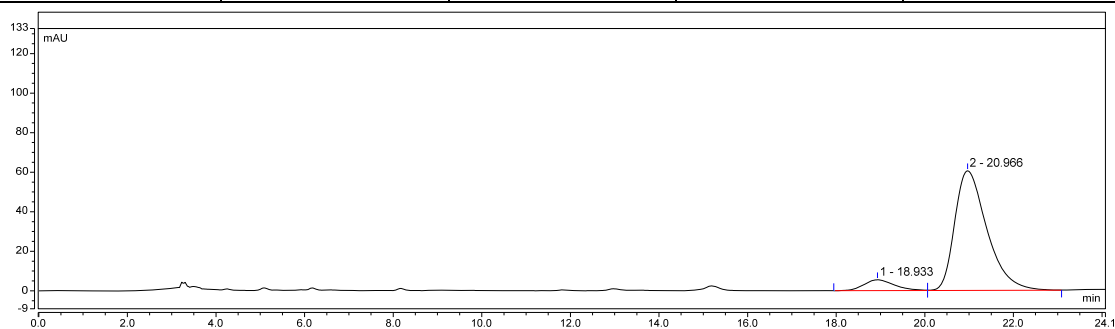


Yellow oil; 34.6 mg, 80% yield; 85% ee;  $[\alpha]_D^{22} -19.5$  (c 1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.1$  Hz, 1H), 7.32 (t,  $J = 8.2$  Hz, 1H), 7.18 (d,  $J = 8.1$  Hz, 1H), 6.74 – 6.63 (m, 3H), 4.13 (m, 2H), 3.83 (s, 1H), 3.73 (s, 3H), 3.52 (d,  $J = 12.9$  Hz, 1H), 2.11 (s, 3H), 1.62 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 153.0, 148.6, 141.9, 139.1, 131.7, 131.5, 126.3, 126.1, 124.0, 116.9, 114.0, 113.5, 111.7, 85.4, 75.5, 55.7, 49.3, 28.1, 17.8; HRMS (ESI)  $m/z$  433.1546 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{Cl}$  433.1530.

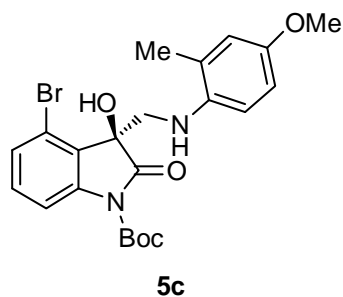
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 18.9 min (minor) and 21.0 min (major).



Entry	Retention Time	Area	Height	%Area
1	18.728	36.3839	46.09	50.90
2	20.999	35.0914	39.78	49.10

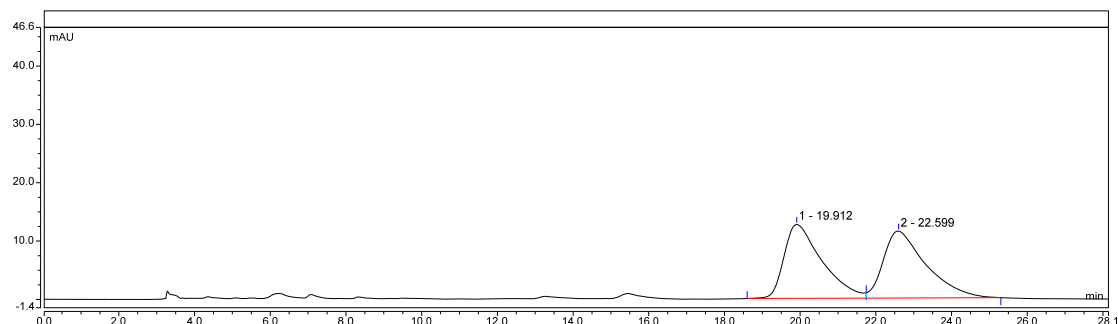


Entry	Retention Time	Area	Height	%Area
1	18.933	4.1145	5.36	7.46
2	20.966	51.0292	60.49	92.54

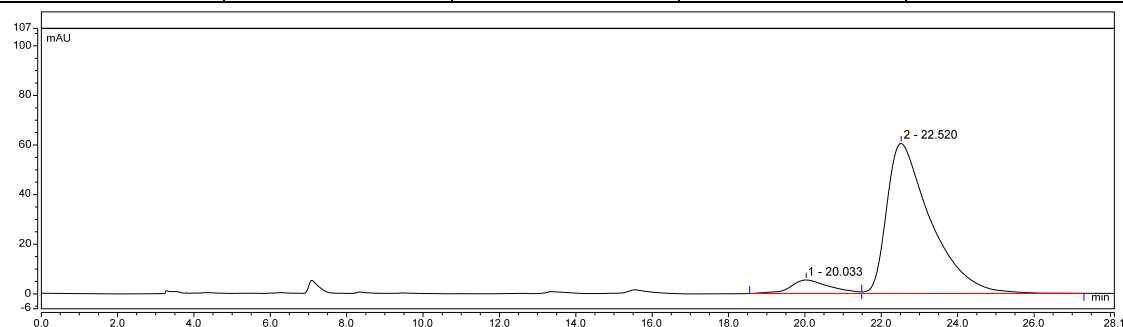


Yellow oil; 36.8 mg, 77% yield; 85% ee;  $[\alpha]_D^{22} -31.8$  (c 2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.1$  Hz, 1H), 7.35 (d,  $J = 8.1$  Hz, 1H), 7.25 – 7.19 (m, 1H), 6.74 – 6.61 (m, 3H), 4.14 (d,  $J = 12.7$  Hz, 1H), 4.08 (s, 1H), 3.77 (s, 1H), 3.72 (s, 3H), 3.52 (d,  $J = 12.9$  Hz, 1H), 2.10 (s, 3H), 1.60 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 153.0, 148.5, 142.0, 139.0, 131.7, 129.5, 126.1, 125.5, 119.4, 116.9, 114.5, 113.6, 111.7, 85.4, 75.9, 55.7, 49.2, 28.1, 17.8; HRMS (ESI)  $m/z$  477.1033 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{Br}_1$  477.1025.

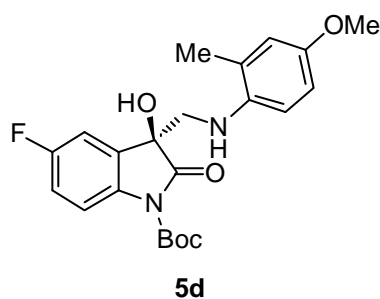
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 20.0 min (minor) and 22.5 min (major).



Entry	Retention Time	Area	Height	%Area
1	19.912	14.6965	12.67	49.56
2	22.599	14.9578	11.47	50.44

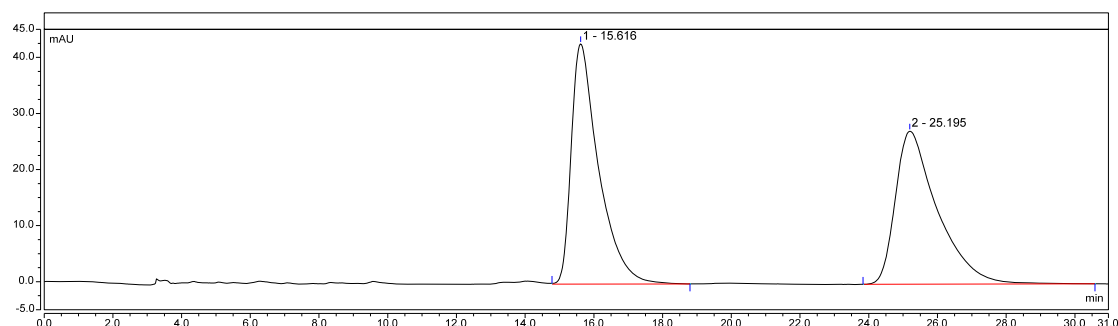


Entry	Retention Time	Area	Height	%Area
1	20.033	6.5428	5.48	7.53
2	22.520	80.3687	60.46	92.47

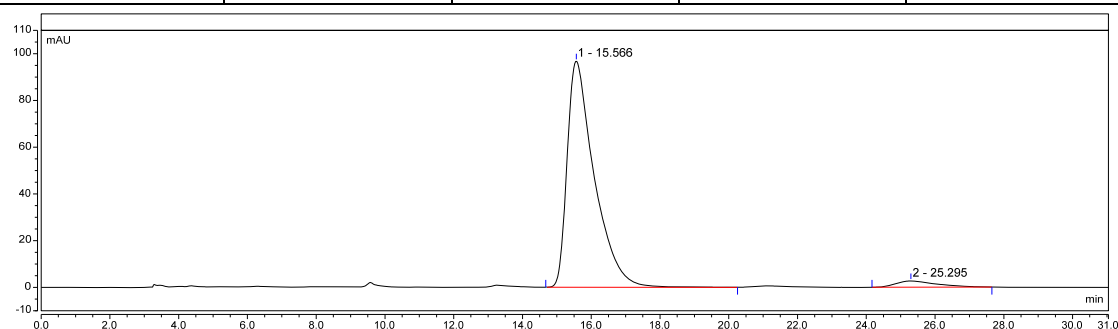


Yellow oil; 36.6 mg, 88% yield; 92% ee;  $[\alpha]_D^{22} +122.6$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (m, 1H), 7.22 (m, 1H), 7.09 (m, 1H), 6.74 – 6.56 (m, 3H), 3.74 (s, 3H), 3.57 (d,  $J = 12.8$  Hz, 1H), 3.35 (d,  $J = 12.7$  Hz, 1H), 2.18 (s, 3H), 1.63 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 152.8, 148.8, 139.7, 139.2, 130.5, 127.5, 126.1, 125.2, 124.7, 116.9, 115.4, 112.9, 111.5, 84.9, 74.3, 55.7, 52.0, 28.1, 17.8; HRMS (ESI)  $m/z$  417.1840 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{F}_1$  417.1826.

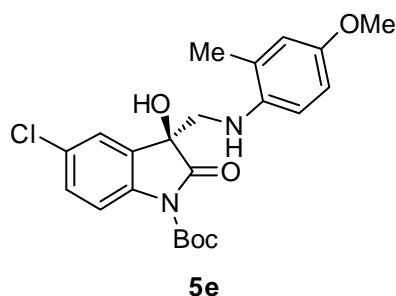
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.6 min (major) and 25.3 min (minor).



Entry	Retention Time	Area	Height	%Area
1	15.616	39.5710	42.84	50.55
2	25.195	38.7168	27.29	49.45

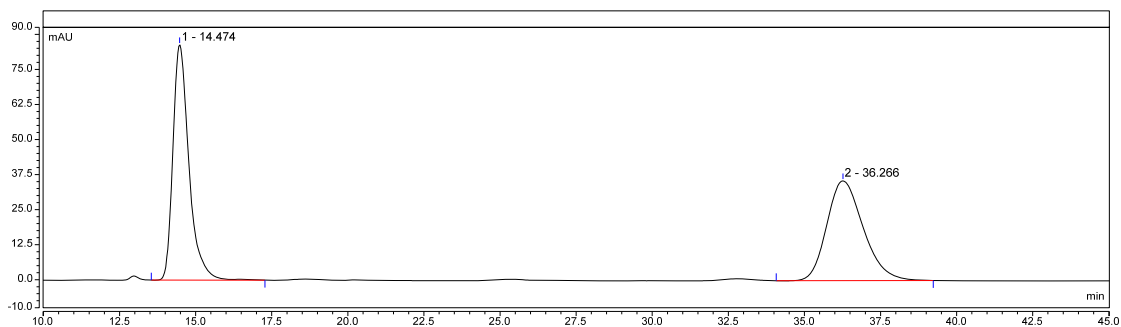


Entry	Retention Time	Area	Height	%Area
1	15.566	88.2816	96.75	95.98
2	25.295	3.6957	2.69	4.02

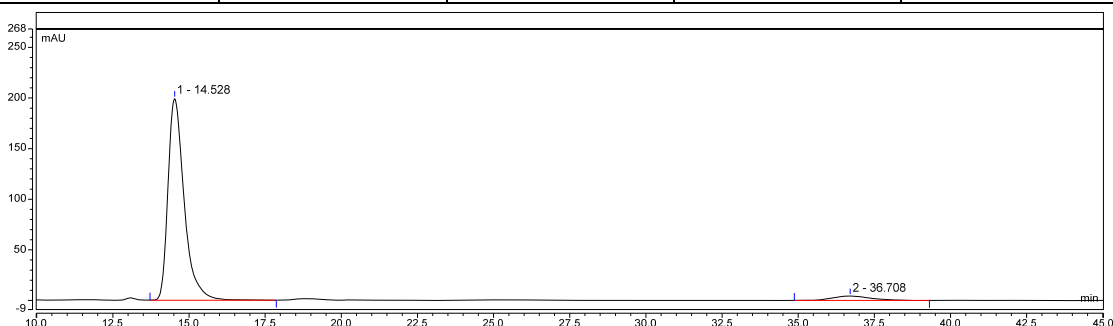


Yellow oil; 38.1 mg, 88% yield; 90% ee;  $[\alpha]_D^{22} +20.3$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.7$  Hz, 1H), 7.46 (d,  $J = 2.0$  Hz, 1H), 7.37 (m, 1H), 6.77 – 6.58 (m, 3H), 4.21 (s, 1H), 3.96 (s, 1H), 3.74 (s, 3H), 3.58 (d,  $J = 13.0$  Hz, 1H), 3.34 (d,  $J = 12.8$  Hz, 1H), 2.19 (s, 3H), 1.63 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0, 153.2, 148.7, 139.1, 138.3, 130.8, 130.6, 129.3, 126.4, 124.6, 117.1, 116.9, 113.7, 111.7, 85.4, 74.2, 55.8, 52.2, 28.2, 17.9.

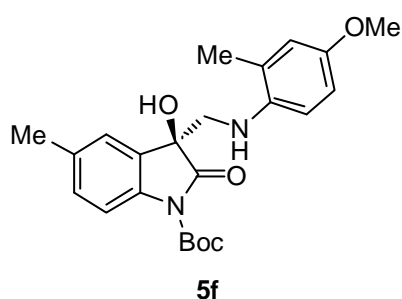
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 14.5 min (major) and 36.7 min (minor) ; HRMS (ESI)  $m/z$  433.1543 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{Cl}$  433.1530.



Entry	Retention Time	Area	Height	%Area
1	14.474	51.2996	83.88	51.00
2	36.266	49.2937	35.56	49.00

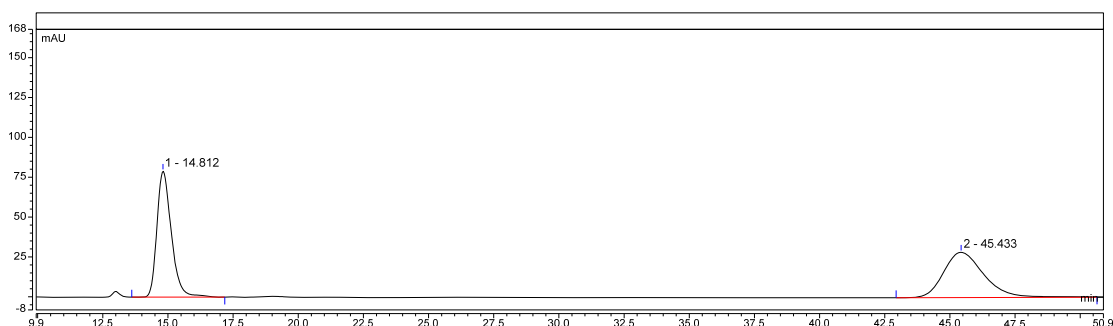


Entry	Retention Time	Area	Height	%Area
1	14.528	122.5667	199.26	95.14
2	36.708	6.2564	4.39	4.86

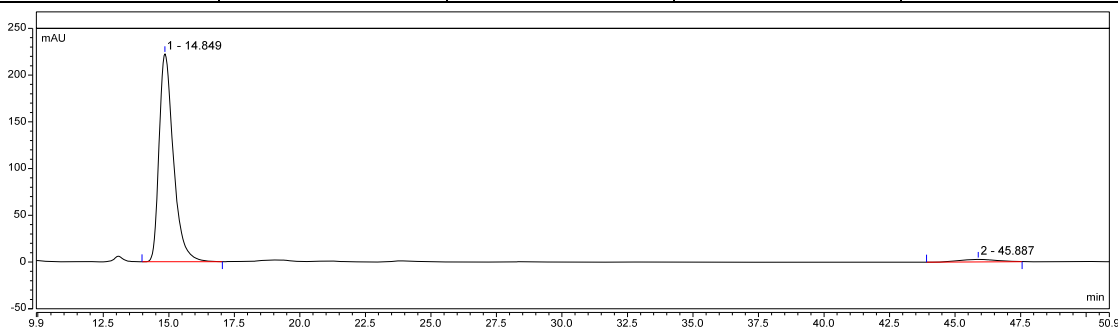


Yellow solid; Mp 46.0 – 47.5 °C; 42.0 mg, 88% yield; 94% ee;  $[\alpha]_D^{22} -9.7$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.52 (m, 1H), 6.73 – 6.59 (m, 3H), 3.74 (s, 3H), 3.58 (d, *J* = 12.8 Hz, 1H), 3.34 (d, *J* = 12.8 Hz, 1H), 2.19 (s, 3H), 1.62 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 175.9, 153.2, 148.7, 139.0, 138.8, 133.5, 129.6, 127.5, 126.4, 118.2, 117.2, 117.1, 113.2, 111.6, 85.4, 74.1, 55.8, 52.1, 28.1, 17.9; HRMS (ESI) *m/z* 477.1031 (M+H<sup>+</sup>), calc. for C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>Br<sub>1</sub> 477.1025.

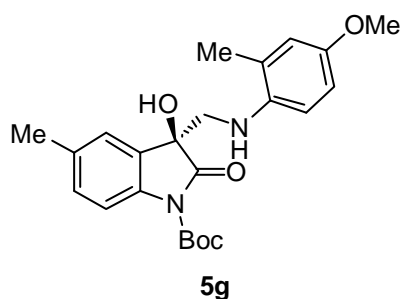
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 14.8 min (major) and 45.9 min (minor).



Entry	Retention Time	Area	Height	%Area
1	14.812	50.6193	78.92	49.83
2	45.433	50.9635	28.35	50.17



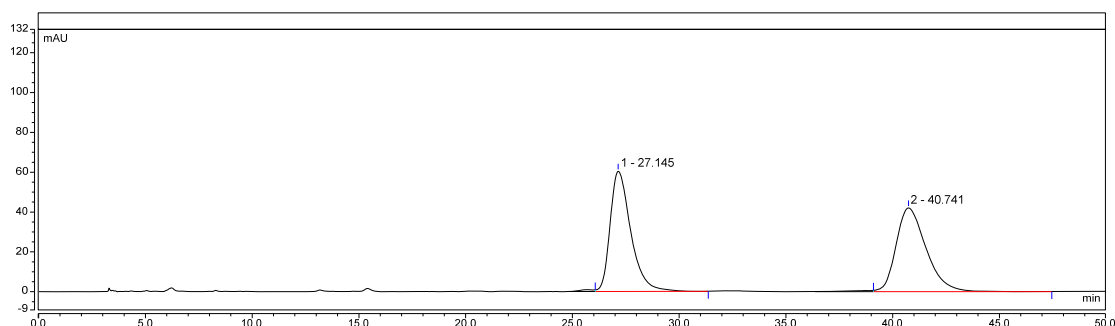
Entry	Retention Time	Area	Height	%Area
1	14.849	140.4197	222.58	97.07
2	45.887	4.2318	2.64	2.93



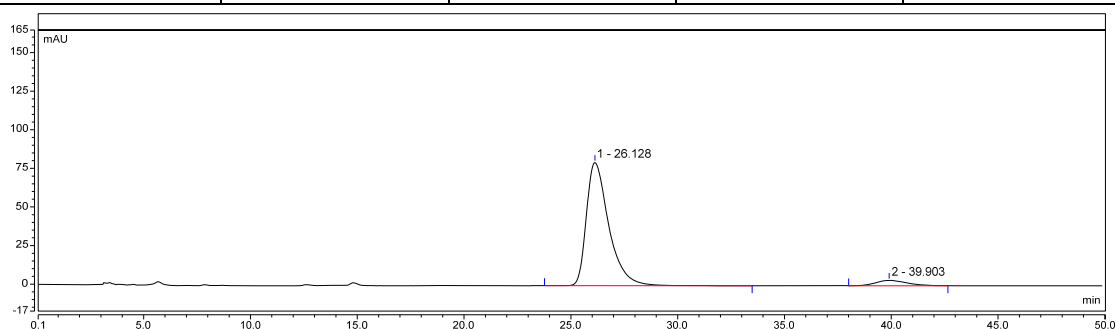
Yellow solid; Mp 49.6 – 50.8 °C; 37.5 mg, 91% yield; 90% ee;  $[\alpha]_D^{22} +51.3$  (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.3 Hz, 1H), 7.29 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.73 – 6.59 (m, 3H), 4.19 (s, 1H), 4.00 (s, 1H), 3.74 (s, 3H), 3.62 (d, *J* = 10.9 Hz, 1H), 3.31 (d, *J* = 12.6 Hz, 1H), 2.37 (s, 3H), 2.17 (s, 3H), 1.63 (s, 9H); <sup>13</sup>C

NMR (75 MHz, CDCl<sub>3</sub>) δ 176.9, 153.0, 148.9, 139.4, 137.4, 135.0, 131.0, 127.4, 126.2, 124.7, 117.0, 115.3, 113.0, 111.6, 84.8, 74.2, 55.8, 52.1, 28.2, 21.1, 17.9; HRMS (ESI) *m/z* 413.2074 (M+H<sup>+</sup>), calc. for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sub>5</sub> 413.2076.

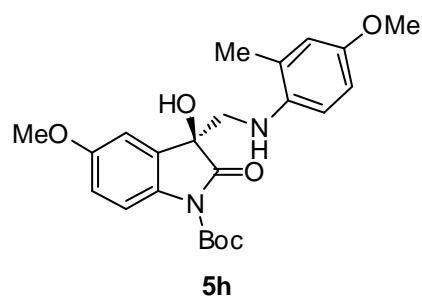
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 26.1 min (major) and 39.9 min (minor).



Entry	Retention Time	Area	Height	%Area
1	27.145	67.3818	60.31	49.72
2	40.741	68.1531	42.04	50.28

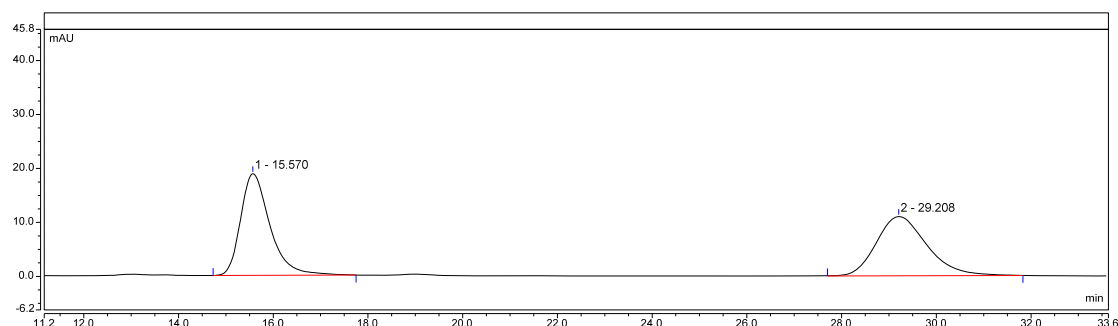


Entry	Retention Time	Area	Height	%Area
1	26.128	96.9323	79.82	94.90
2	39.903	5.2086	3.33	5.10

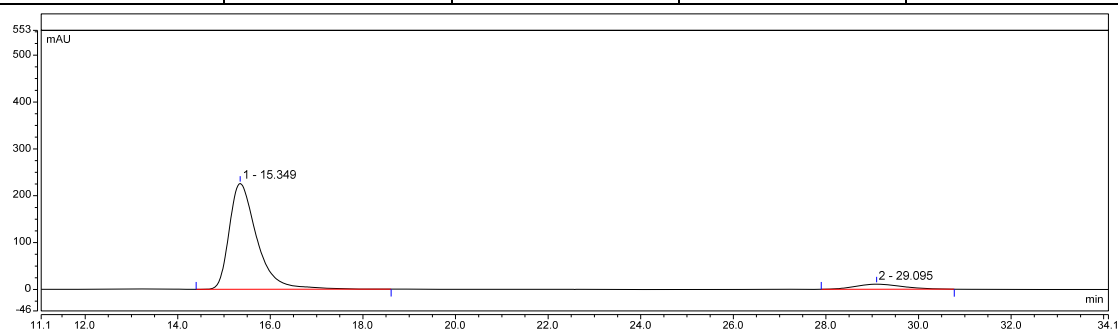


Yellow oil; 38.6 mg, 90% yield; 85% ee;  $[\alpha]_D^{22} +59.4$  ( $c$  2.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J$  = 8.9 Hz, 1H), 7.04 (d,  $J$  = 2.5 Hz, 1H), 6.91 (dd,  $J$  = 8.9, 2.6 Hz, 1H), 6.71 – 6.57 (m, 3H), 4.21 (s, 1H), 3.96 (s, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.59 (d,  $J$  = 12.7 Hz, 1H), 3.33 (d,  $J$  = 12.6 Hz, 1H), 2.16 (s, 3H), 1.62 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 157.4, 152.9, 148.9, 139.3, 132.9, 128.7, 126.1, 117.0, 116.6, 115.7, 112.9, 111.6, 109.9, 84.8, 74.6, 55.8, 55.7, 52.2, 28.2, 17.8; HRMS (ESI)  $m/z$  429.2028 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_6$  429.2026.

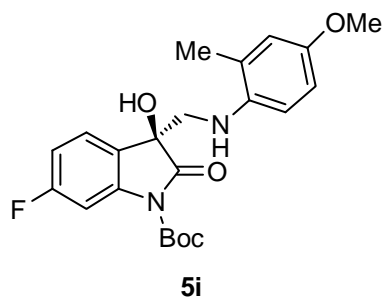
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 15.3 min (major) and 29.1 min (minor).



Entry	Retention Time	Area	Height	%Area
1	15.570	13.5298	18.84	49.96
2	29.208	13.5524	10.97	50.04



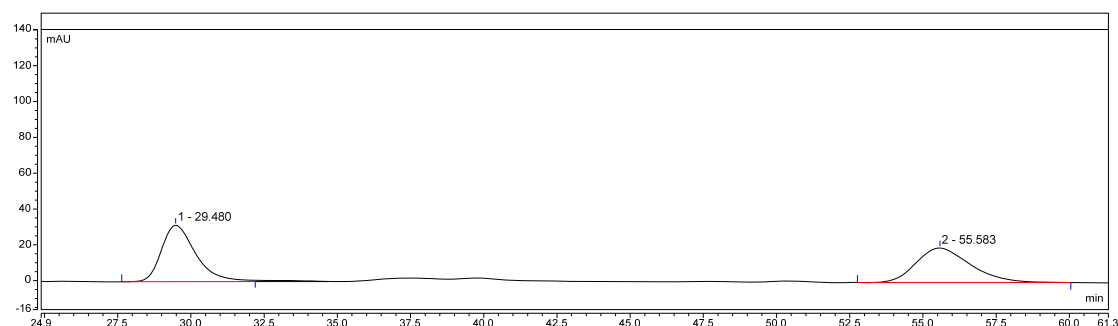
Entry	Retention Time	Area	Height	%Area
1	15.349	155.8772	225.67	92.44
2	29.095	12.7394	10.81	7.56



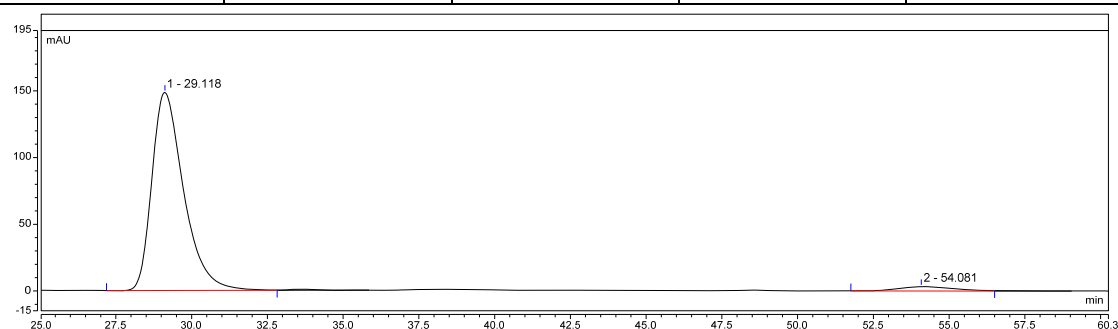
Yellow oil; 30.8 mg, 74% yield; 93% ee;  $[\alpha]_D^{22} +164.6$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (dd,  $J = 10.2, 2.3$  Hz, 1H), 7.44 (dd,  $J = 8.3, 5.6$  Hz, 1H), 6.92 (m, 1H), 6.70 – 6.57 (m, 3H), 3.74 (s, 3H), 3.58 (d,  $J = 12.8$  Hz, 1H), 3.34 (d,  $J = 12.8$  Hz, 1H), 2.17 (s, 3H), 1.63 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 165.7, 162.5, 153.3, 148.8, 141.4, 141.2, 139.3, 126.4, 125.7, 125.6, 123.3, 123.2, 117.2, 113.3, 112.2, 111.9, 111.8, 104.8, 104.4, 85.6, 74.2, 55.9, 52.4, 28.3, 18.0; HRMS (ESI)  $m/z$  417.1832 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{F}_1$  417.1826.

The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 29.1 min (major) and 54.1 min (minor).

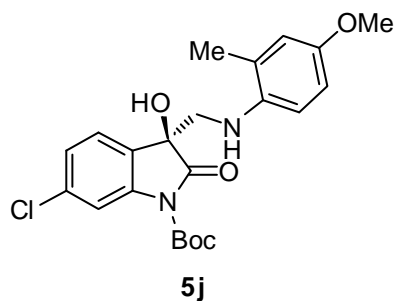




Entry	Retention Time	Area	Height	%Area
1	29.480	42.6606	31.50	50.76
2	55.583	41.3819	19.29	49.24



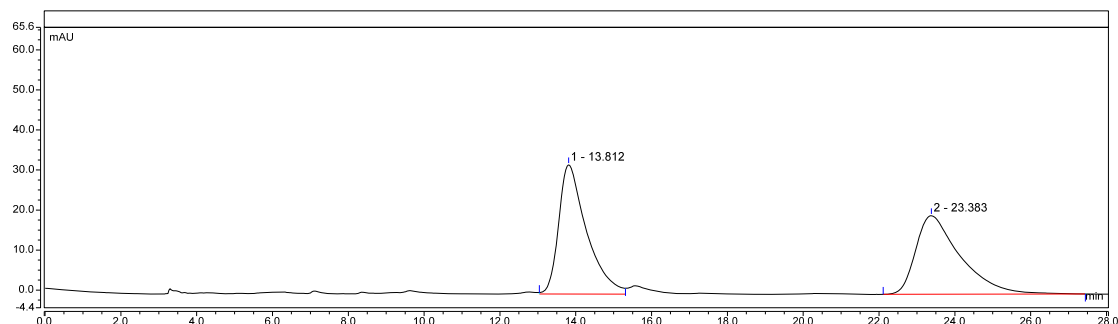
Entry	Retention Time	Area	Height	%Area
1	29.118	180.5570	148.50	96.45
2	54.081	6.6459	3.21	3.55



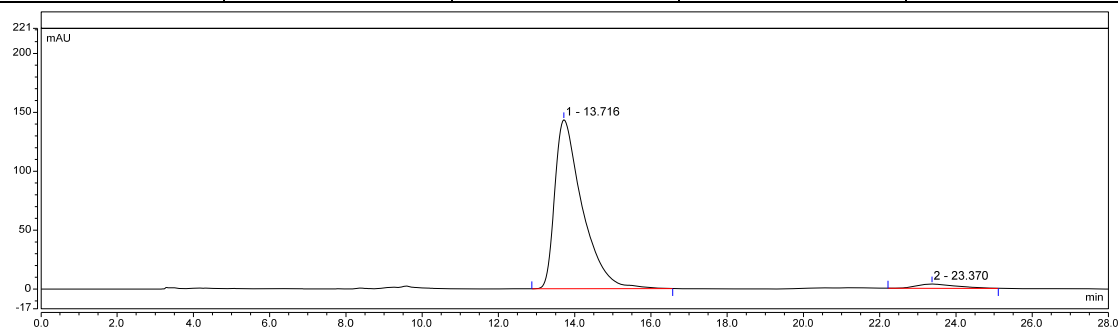
Yellow oil; 32.9 mg, 76% yield; 93% ee;  $[\alpha]_D^{22} +12.2$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 1.7 Hz, 1H), 7.41 (d,  $J$  = 8.0 Hz, 1H), 7.21 (dd,  $J$  = 8.0, 1.7 Hz, 1H), 6.70 – 6.57 (m, 3H), 3.73 (s, 3H), 3.57 (d,  $J$  = 12.8 Hz, 1H), 3.34 (d,  $J$  = 12.8 Hz, 1H), 2.17 (s, 3H), 1.63 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 153.1.

148.7, 140.7, 139.1, 136.4, 126.3, 126.0, 125.3, 125.2, 117.0, 116.3, 113.2, 111.7, 85.5, 74.1, 55.8, 52.2, 28.1, 17.9; HRMS (ESI)  $m/z$  433.1517 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{Cl}_1$  433.1530.

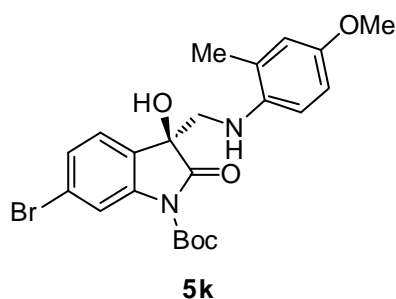
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 13.7 min (major) and 23.4 min (minor).



Entry	Retention Time	Area	Height	%Area
1	13.812	27.4522	32.26	50.67
2	23.383	26.7208	19.62	49.33

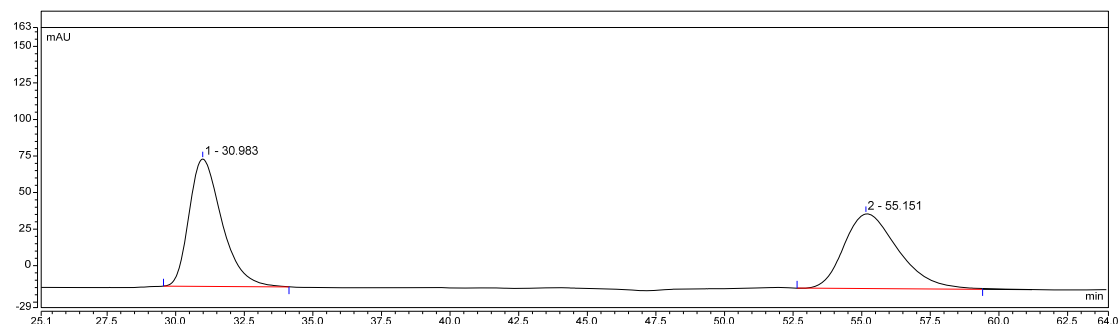


Entry	Retention Time	Area	Height	%Area
1	13.716	119.4245	143.33	96.48
2	23.370	4.3589	3.62	3.52

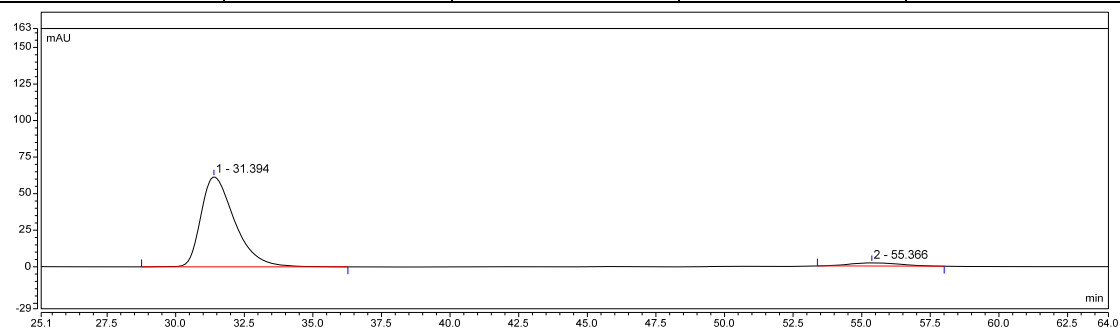


Yellow oil; 37.2 mg, 78% yield; 90% ee;  $[\alpha]_D^{22} +124.4$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J$  = 0.8 Hz, 1H), 7.40 – 7.32 (m, 2H), 6.70 – 6.56 (m, 3H), 3.73 (s, 3H), 3.56 (d,  $J$  = 12.8 Hz, 1H), 3.33 (d,  $J$  = 12.8 Hz, 1H), 2.17 (s, 3H), 1.63 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 153.1, 148.6, 140.8, 139.1, 128.2, 126.5, 126.3, 125.5, 124.3, 119.1, 117.0, 113.2, 111.6, 85.6, 74.2, 55.8, 52.1, 28.1, 17.9; HRMS (ESI)  $m/z$  477.1027 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5\text{Br}_1$  477.1025.

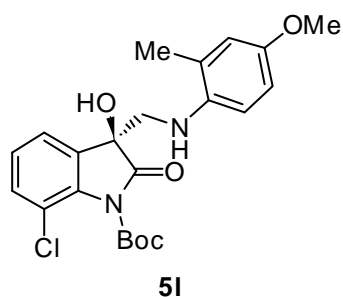
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 95/5; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 31.4 min (major) and 55.4 min (minor).



Entry	Retention Time	Area	Height	%Area
1	30.983	120.8333	87.18	50.80
2	55.151	117.0261	51.20	49.20

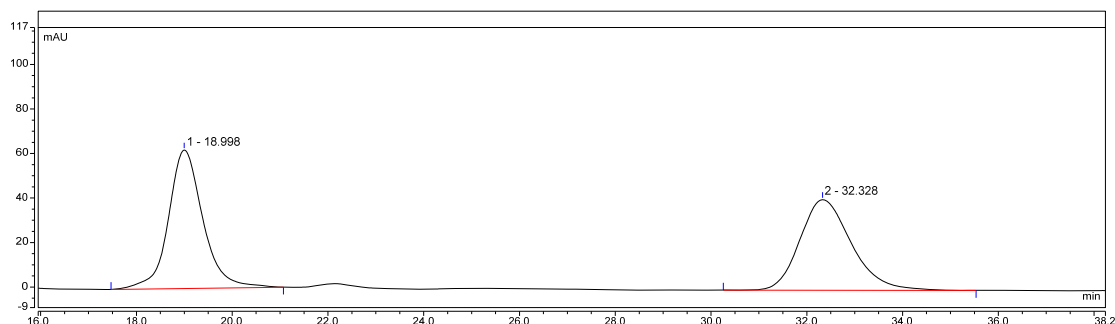


Entry	Retention Time	Area	Height	%Area
1	31.394	87.8359	61.45	94.95
2	55.366	4.6720	2.25	5.05

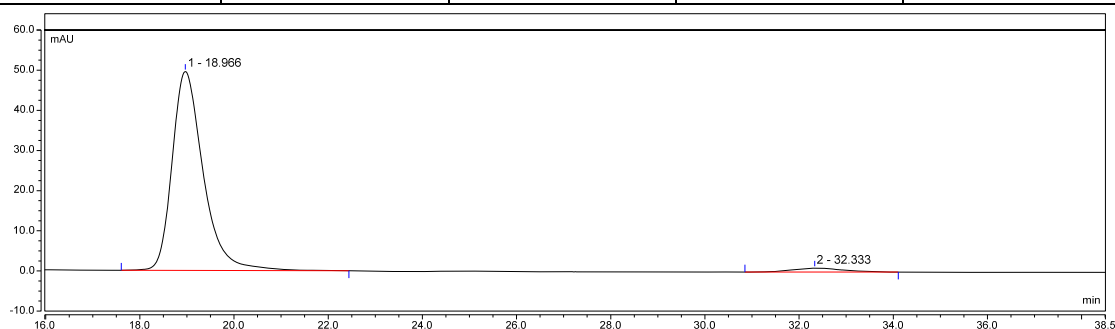


Yellow solid; Mp 68.1 – 69.7 °C; 31.6 mg, 73% yield; 94% ee;  $[\alpha]_D^{22}$  -173.6 (c 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.46 – 7.31 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.72 – 6.57 (m, 3H), 3.74 (s, 3H), 3.58 (d, *J* = 12.7 Hz, 1H), 3.36 (d, *J* = 12.8 Hz, 1H), 2.19 (s, 3H), 1.62 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 176.6, 153.2, 147.6, 139.2, 137.0, 132.2, 131.0, 126.4, 125.9, 122.8, 119.3, 117.1, 113.1, 111.7, 86.1, 75.2, 55.8, 52.1, 27.8, 17.9; HRMS (ESI) *m/z* 433.1518 (M+H<sup>+</sup>), calc. for C<sub>22</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>Cl<sub>1</sub> 433.1530.

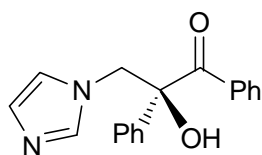
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.0 min (major) and 32.3 min (minor).



Entry	Retention Time	Area	Height	%Area
1	18.998	51.9690	62.20	50.68
2	32.328	50.5766	40.73	49.32



Entry	Retention Time	Area	Height	%Area
1	18.966	37.9154	49.55	97.03
2	32.333	1.1588	0.97	2.97

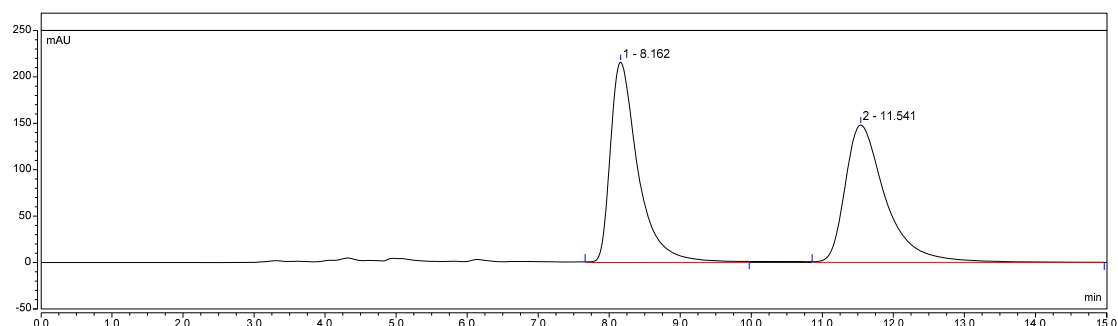


7

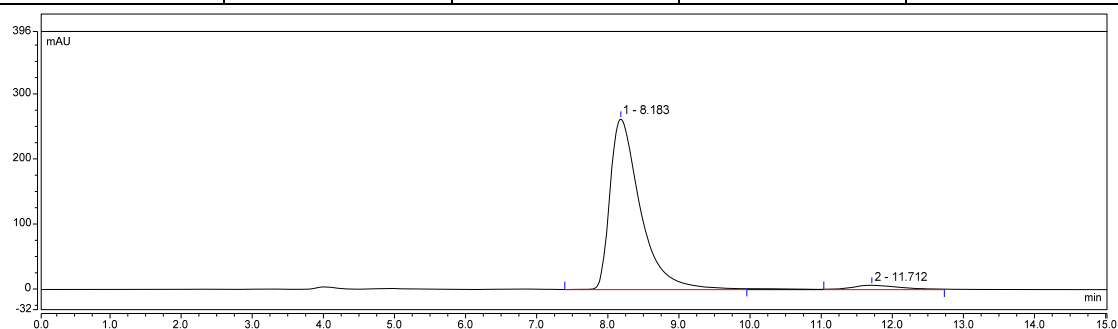
White solid; Mp 164.1 – 165.7 °C; 76.0 mg, 65% yield; 92% ee;  $[\alpha]_{\text{D}}^{22}$  +54.2 (c 0.5, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, DMSO) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.24 (m, 6H), 7.14 (s, 1H), 7.05 (s, 1H), 6.68 (d, *J* = 4.1 Hz, 2H), 4.57 (q, *J* = 14.3 Hz, 2H); <sup>13</sup>C

NMR (75 MHz, DMSO) δ 199.3, 139.2, 138.2, 134.3, 132.9, 130.2, 128.5, 128.1, 127.8, 127.0, 124.8, 120.8, 81.5, 54.9; HRMS (ESI) *m/z* 293.1283 (M+H<sup>+</sup>), calc. for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> 293.1285.

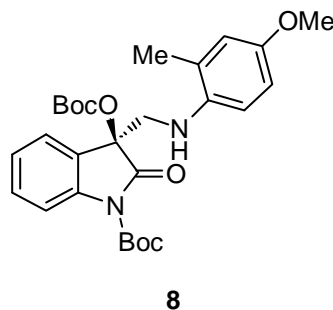
The ee was determined by HPLC analysis: CHIRALPAK OZ-H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 8.2 min (major) and 11.7 min (minor).



Entry	Retention Time	Area	Height	%Area
1	8.162	97.3371	215.84	49.91
2	11.541	97.6848	148.08	50.09

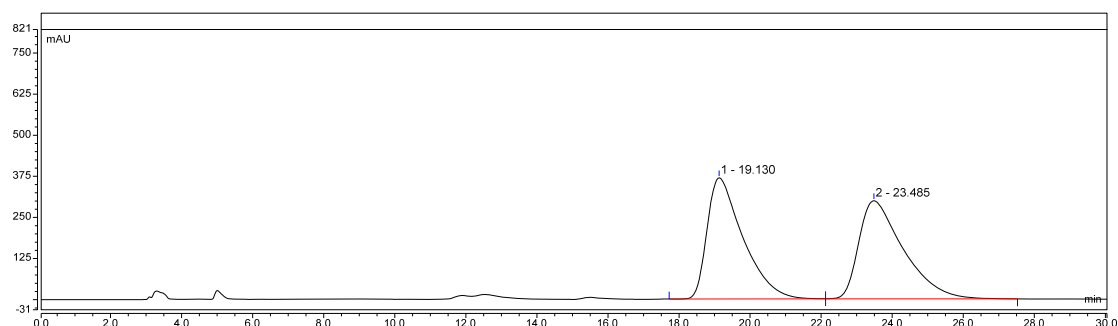


Entry	Retention Time	Area	Height	%Area
1	8.183	129.8393	262.04	96.14
2	11.712	5.2069	6.70	3.86

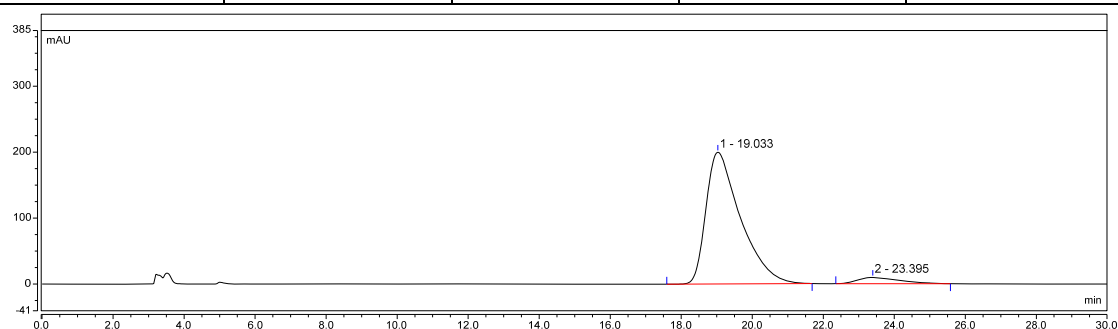


Yellow oil; 195.4 mg, 98% yield; 91% ee;  $[\alpha]_D^{22} +125.0$  (c 0.5,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.2$  Hz, 1H), 7.39 (t,  $J = 7.4$  Hz, 2H), 7.18 (t,  $J = 7.5$  Hz, 1H), 6.65 – 6.54 (m, 2H), 6.43 (d,  $J = 8.5$  Hz, 1H), 3.77 (d,  $J = 13.0$  Hz, 1H), 3.69 (s, 3H), 3.60 (d,  $J = 13.0$  Hz, 1H), 3.37 (s, 1H), 1.99 (s, 3H), 1.61 (s, 9H), 1.36 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0, 152.3, 150.7, 148.8, 140.3, 139.2, 130.5, 125.6, 124.8, 123.0, 116.7, 115.5, 112.4, 111.5, 84.6, 84.3, 79.8, 55.7, 51.1, 28.1, 27.6, 17.6; HRMS (ESI)  $m/z$  499.2449 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{27}\text{H}_{35}\text{N}_2\text{O}_7$  499.2444.

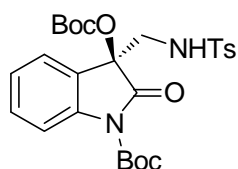
The ee was determined by HPLC analysis: CHIRALPAK OZ-H (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 19.0 min (major) and 23.4 min (minor).



Entry	Retention Time	Area	Height	%Area
1	19.130	430.6204	368.03	49.86
2	23.485	433.0109	298.34	50.14



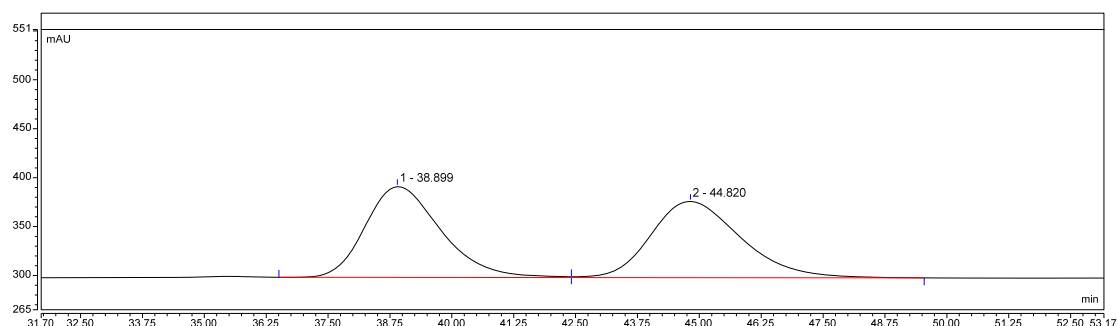
Entry	Retention Time	Area	Height	%Area
1	19.033	224.8855	199.81	95.35
2	23.395	10.9649	9.10	4.65



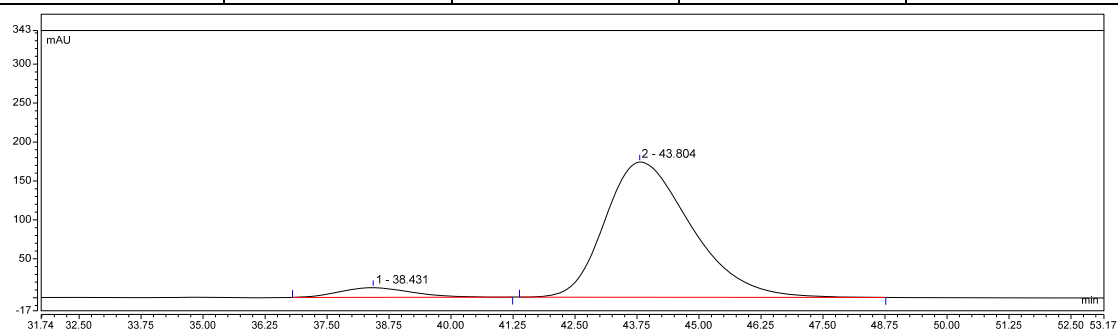
**9**

White solid; Mp 87.4 – 88.5 °C; 153.4 mg, 72% yield; 91% ee;  $[\alpha]_D^{22}$  –24.6 (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 5.09 (s, 1H), 3.52 – 3.26 (m, 2H), 2.39 (s, 3H), 1.62 (s, 9H), 1.29 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.1, 149.2, 147.6, 142.7, 138.9, 135.6, 129.8, 128.9, 126.1, 124.0, 123.3, 122.7, 114.5, 84.1, 83.6, 77.3, 47.5, 27.1, 26.5, 20.6; HRMS (ESI) *m/z* 533.1961 (M+H<sup>+</sup>), calc. for C<sub>26</sub>H<sub>33</sub>N<sub>2</sub>O<sub>8</sub>S<sub>1</sub> 533.1958.

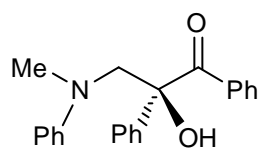
The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25 °C; 210 nm; retention time: 38.4 min (major) and 43.8 min (minor).



Entry	Retention Time	Area	Height	%Area
1	38.899	164.1968	92.82	50.04
2	44.820	163.9251	77.89	49.96

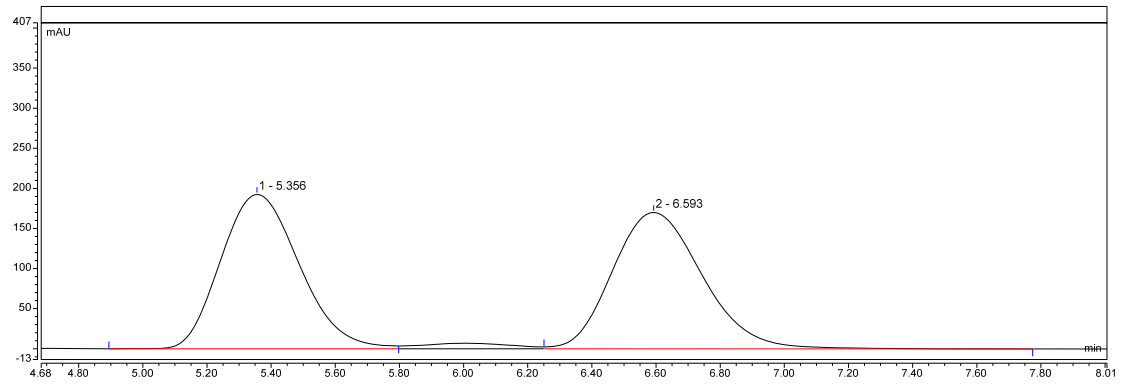


Entry	Retention Time	Area	Height	%Area
1	38.431	17.1494	11.40	4.67
2	43.804	349.8591	173.60	95.33

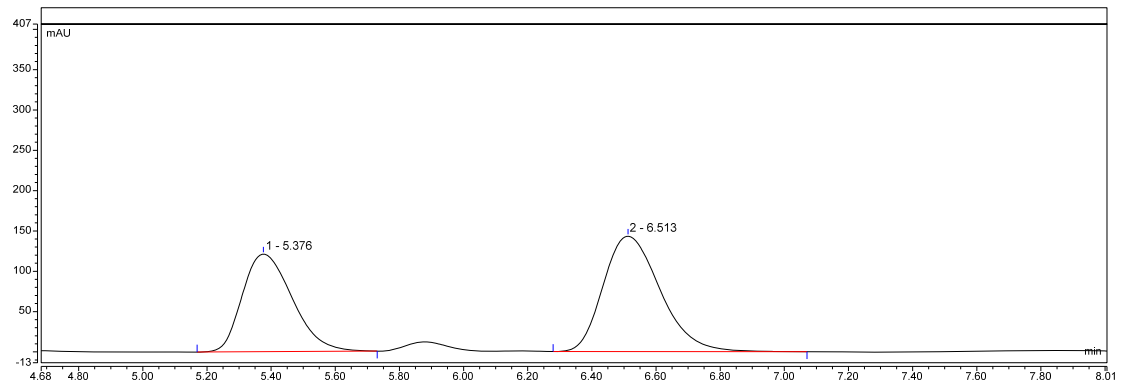
**11**

Yellow oil; 11.6 mg, 35% yield; 15% ee;  $[\alpha]_D^{22} +8.1$  (*c* 0.5,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 7.7$  Hz, 2H), 7.57 (d,  $J = 7.5$  Hz, 2H), 7.47 – 7.29 (m, 4H), 7.25 – 7.11 (m, 4H), 6.80 (m, 3H), 4.44 (d,  $J = 14.6$  Hz, 1H), 4.30 (s, 1H), 3.53 (d,  $J = 14.6$  Hz, 1H), 2.67 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 141.7, 135.37, 135.07, 132.8, 130.7, 130.1, 129.3, 129.1, 128.1, 128.0, 124.8, 115.1, 82.1, 64.0, 34.0; HRMS (ESI)  $m/z$  332.1642 ( $\text{M}+\text{H}^+$ ), calc. for  $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2$  332.1645.

The ee was determined by HPLC analysis: CHIRALPAK IC (4.6 mm i.d. x 250 mm); Hexane/2-propanol = 97/3; flow rate 1.0 mL/min; 25 °C; 254 nm; retention time: 5.3 min (minor) and 6.5 min (major).



Entry	Retention Time	Area	Height	%Area
1	5.356	54.6084	192.47	49.69
2	6.593	55.2937	170.06	50.31



Entry	Retention Time	Area	Height	%Area
1	5.376	21.7741	120.98	42.51
2	6.513	29.4453	143.04	57.49



## 8. Copies of NMR spectra

